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THE

# CHEMICAL NEWS

AND

## JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

## A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

## PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

*WILLIAM CROOKES, F.R.S., &c.*

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# THE CHEMICAL NEWS.

VOLUME LV.

*EDITED BY WILLIAM CROOKES, F.R.S., &c.*

No. 1415.—JANUARY 7, 1887.

## ON COHESION AND SUBMERSION FIGURES.

By CHARLES TOMLINSON, F.R.S., F.C.S.

In the CHEMICAL NEWS (vol. liv., p. 58, July, 1886) is an abstract of a lecture delivered by Mr. William Ackroyd, F.I.C., before the Halifax Scientific Society, in July last, in which it is stated that when a liquid drop descends below the surface of water, and assumes a ring shape which gradually spreads out, and breaks up into lesser rings, such figures are not "submergence cohesion figures," as they have been called, but vortex rings. In the abstract of this notice, given in the *Journal of the Chemical Society* for December last, the author is said to justify the above notion by comparing the conditions of formation of aërial and of liquid vortex rings, and showing their resemblance.

In 1861 I introduced the subject of the cohesion figures of liquids to the British Association at its meeting in Manchester, and exhibited a large number of figures; and at the meeting at Bath in 1864 other figures, modified by the various surfaces on which they were exhibited, were shown, together with a new set of figures under the name of "Submersion Figures." In addition to the brief notices in the *British Association Reports*, full descriptions, with illustrative engravings, were inserted in the *Philosophical Magazine* and elsewhere. The subject has since been taken up by Mr. Worthington, Messrs. J. J. Thomson and Newall, and others.

I may remark that I did not name this second set of figures "Submergence Cohesion Figures," but simply "Submersion Figures," such as, in fact, they really are, and involving no theory as to their formation or structure. I was led to the study of them while preparing a lecture at King's College, when, having occasion for an aqueous solution of cochineal, a number of the insects was crushed in a mortar together with a small quantity of water, and so poured upon a filter standing over a vessel of water. I noticed that as the drops descended beautiful curved lines were formed, and I thus received the suggestion for a new and interesting inquiry. In my first experiments the cochineal figures were greatly improved by mixing a little alum with the water into which the drops were received. Various other liquids besides water contained in cylindrical glasses were used as recipients, and drops of various liquids were also employed. I was not aware at this time that liquid vortex rings had been described; but on showing my results to Professor Miller he informed me that Professor Rogers had a paper on liquid rolling rings in the *American Journal of Science* for September, 1858, and he lent me the copy that he had received from the author.

In my first paper on "Submersion Figures," in the *Phil. Mag.* for June, 1864, an abstract is given of Professor Rogers's paper, and in the plate which accompanies my paper a diagram is given showing a drop on a horizontal line which, descending into a liquid column, forms a liquid rolling ring, the structure of which is given; or, ascending like a bubble of phosphuretted hydrogen, forms an aërial rolling ring, the structure of which is also given. The plate further shows the figures of drops of a dense aqueous solution of cochineal in a column of alum water, and also in one of oxalate of ammonia, oil of lavender in spirit, croton oil in benzole and in paraffin oil, fusel oil in paraffin oil, benzole in ether, oil of bitter almonds in benzole, common salt in water, &c. In subsequent papers (November, 1864, &c.) other figures are represented, such as those formed by drops of sesame, and colza oils in cocoa-nut oil, oil of cloves in castor oil, castor or croton oil in melted lard, croton and cinnamon oils and creosote in a column of olive oil.

At the meeting of the British Association at Edinburgh, in 1871, Mr. H. Deacon, not knowing my results, brought before the Chemical Section some figures that he had obtained by allowing drops of heavy liquids or solutions to fall into a column of water. Before the reading of his paper he was introduced to me, and he showed me the drawings of some of his figures, which I told him were identical with some of mine, and referred him to my papers in the *Phil. Mag.*, which he consulted in the library of the Royal Society of Edinburgh.

At that time some distinguished physicists of Edinburgh were very much interested in the subject of vortex rings, and Professor Clerk Maxwell informed me that he had produced some of my figures by allowing water to fall from a height through the air, from an upper window for example. After the reading of Mr. Deacon's paper, and the exhibition of his figures (which soon after appeared in the CHEMICAL NEWS) there was some discussion as to the best mode of exhibiting vortex rings, aërial and liquid, and I gave some particulars respecting their exhibition at the lecture table.

Professor Daniell, of King's College, was accustomed to exhibit smoke rings by means of a tinned iron cone covered at the base with a parchment head, and furnished at the truncated end with a short tube. On filling this with smoke, and striking the parchment, smoke rings were shot out into the air. About 1842 Dr. Boswell Reid was engaged by the Committee of Council on Education to lecture to some of the charity schools of the metropolis, and the children were accustomed to assemble in Exeter Hall, each school occupying a set of benches by itself, so that the coloured costumes of the

children had an odd effect—the greens in one place, the drabs in another, and so on; but the oddest part of the affair was in the delivering of separate courses of lectures to separate groups. The lecturer might be addressing the greens, for example, giving them half-an-hour or so, and then turning to the greys begin on a new subject to them in continuation of some previous lecture. In this way he got through several lectures in one evening. His apparatus was adapted to the size of the lecture-room and the distance of his pupils from the platform. Thus his apparatus for producing smoke rings was of the size of a large drum, and on striking the parchment head with his fist the lecturer projected a fine smoke ring through the air of the hall. Some years later, on the Emperor's fête day in Paris, splendid smoke rings were produced for the amusement of the populace from the greased mouths of cannon fired with blank cartridge. In the *Annales de Chimie et de Physique*, for 1864, my submersion figures were noticed, and also a box contrived by M. Coulier, from which rings of chloride of ammonium smoke were projected.

But, to return to the liquid vortex rings, Mr. Deacon inserted in this journal a couple of papers, in which he was very angry with me. He quoted largely from Prof. Rogers's paper; but as I had already done full justice to the American physicist, it was not necessary for me to reply.

In 1868, while studying the action of nuclei in liberating vapour from boiling liquids, a curious observation was made. Some oil of turpentine was being heated in a test-tube over the flame of a spirit-lamp. About half way down the tube was a speck of carbon which had apparently become attached while the glass in the process of manufacture was still soft. As soon as the turpentine had reached the boiling point, a series of rapid intermittent vortex rings escaped from the carbon point with such rapidity as to form a low musical note. Each jet consisted of about twelve or fifteen rings expanding upwards from a point. This led me to seek for some numerical values as to the action of porous bodies in liberating vapour from boiling liquids. I take one example from my paper inserted in the *Proceedings of the Royal Society* for January, 1869. Water boiled in a clean flask lost in twenty minutes 995 grains; and again, during the same time, and with the same amount of heat, but with a nucleus of coke in the water, the loss was 1130 grains; the ratio of the products being as 100 : 113·6.

Charcoals made from boxwood and cocoa-nut shell are still more active as nuclei in liberating vapour from a boiling liquid under distillation; while at the same time they prevent the bumping of the vessel.

Highgate, N., January 1st, 1887.

## CHROMIC ACID COMBUSTION OF GLYCERIN.

By C. F. CROSS and E. J. BEVAN.

We have recently noticed the description of a method for the estimation of glycerin (in wines), based upon combustion with chromic acid in presence of concentrated sulphuric acid (L. Legler, *Rep. An. Ch.*, 1886, 6, 631; *Chem. Ztg.*, 1886, 262). The author adopts the gravimetric method of determining the products of combustion. It occurred to us to try this particular combustion according to the volumetric method described by us some time since in the CHEMICAL NEWS, vol. lii., p. 207. The carbon percentage estimated by this method in pure glycerin was 38·7, the theoretical number being 39·1; the method therefore gives satisfactory results in this case as we have found in many others.

For the benefit of those who are in possession of the instrument we would mention that Lunge's nitrometer is well adapted to the purpose. We intend at an early opportunity to give a detailed account of the method as applied to a variety of carbon compounds.

4, New Court, Lincoln's Inn.

## ACIDIMETRIC PROCESS FOR ESTIMATING "CHROMATE" IN PRESENCE OF "BICHROMATE."

By NORMAN McCULLOCH.

Bichromate of soda, as a technical substitute for bichromate of potash, is of rising importance on account of its greater cheapness, strength of chromic acid, and solubility in water; and with improved means of storage to protect it from atmospheric moisture and consequent deliquescence, bids fair to entirely replace it.

In the CHEMICAL NEWS, vol. liv., p. 194, we are favoured by Mr. Arthur Stanley with a few "Properties and Constants" of bichromate of soda.

The usual impurities of the commercial salt are, conveniently speaking, water, chloride of sodium, sulphate of soda, bichromate of potash, and chromate of soda. The analysis of the last-named constituent alone calls for any special comment, and the subject of this communication is a convenient process for its estimation.

A method for directly determining chromate in presence of bichromate has not so far, to my knowledge, been suggested, and consequently the most approved procedure for analysing such mixtures consists in the direct estimation of the bichromate by titration with standard caustic alkali in presence of phenolphthalein, until by its complete conversion into normal chromate, with slight excess of alkali, the reddish yellow of the solution changes to a yellowish red; and after subtracting the chromic acid equivalent of the bichromate so found from the total chromic acid as estimated with ferrous salt we have as a remainder the chromic acid existing in the sample as chromate.

The results are fairly satisfactory, but the method has a practical drawback in the fact that the exact conversion of the bichromate into the normal salt is not defined by the phenol phthalein with sufficient sharpness, and the operator in standardising his caustic alkali with pure potassium bichromate must hit a degree of neutral tint to be rigidly adhered to in titrating unknown quantities.

In devising a process superior to the above I have taken advantage of the fact that neither bichromate nor chromate yield to a mixture of peroxide of hydrogen and ether the well known blue colouration of chromium heptoxide peculiar under these circumstances to free chromic acid, and in the case of chromate the phenomenon develops only with the addition of such a quantity of acid as is slightly in excess of that necessary to completely convert the chromate into bichromate.

To apply these facts to practical work, 5 or 10 grms. of the sample are placed in a test-tube 4 centimetres in diameter and ¼ metre or so in length, and dissolved in a small quantity of water. A few c.c. of peroxide of hydrogen (10 vols.) are added, and the whole covered with a layer of sulphuric ether 3 centimetres in depth. The mouth of the test-tube is now stopped with a paraffined cork pierced in the centre with a short glass tube for admitting the standard sulphuric acid, which is run in from a burette in small quantities at a time, with agitation after each addition, until the layer of ether is tinged faintly blue as best seen against a white background. By calculating the equivalent of acid consumed to two equivalents of chromate of soda or potash, as the case may be, we obtain the chromate in the portion of the sample taken.

Judging from the very dark colour that peroxide of

*Value of Test-Acid, calc. from Expts.* 1 *and* 2. C.c.=0·0113 grm. $Na_2CO_3$=0·4148 grm. $K_2CrO_4$.
" " " 4 *and* 5. C.c.=0·011236 " " 0·4124 " "

| No. of Expt. | Indicator. | Material and the quantity used. | C.c. of Test-Acid added. | Quantity found, calc. from 1 and 2. | Quantity found, calc. from 4 and 5. |
|---|---|---|---|---|---|
| 1. | Litmus | 1·6197 grms. $Na_2CO_3$ | 143·34 | — | — |
| 2. | Litmus | 1·6197 grms. $Na_2CO_3$ | 143·34 | — | — |
| 3. | $H_2O_2$ and ether | 1·6197 grms. $Na_2CO_3$+0·32 grm. $K_2Cr_2O_7$ | 143·99 | 1·6268 | — |
| 4. | Ditto | 1·6197 grms. $Na_2CO_3$+1·62 grms. $K_2Cr_2O_7$ | 144·15 | 1·6288 | — |
| 5. | Ditto | 0·6479 grm. $Na_2CO_3$+3·2 grms. $K_2Cr_2O_7$ | 57·66 | 0·6511 | — |
| 6. | Ditto | 3·2394 grms. $K_2CrO_4$ | 78·20 | 3·2433 | 3·2245 |
| 7. | Ditto | 3·2394 grms. $K_2CrO_4$ | 78·39 | 3·2518 | 3·2330 |
| 8. | Ditto | 3·2394 grms. $K_2CrO_4$ | 78·33 | 3·2485 | 3·2297 |
| 9. | Ditto | 0·6479 grm. $K_2CrO_4$+3·24 grms. $K_2Cr_2O_7$ | 15·73 | 0·6524 | 0·6491 |
| 10. | Ditto | 0·01296 grm. $K_2CrO_4$+3·24 grms. $K_2Cr_2O_7$ | 0·32 | 0·1295 | 0·1295 |
| 11. | Ditto | 0·00648 grm. $K_2CrO_4$+3·24 grms. $K_2Cr_2O_7$ | 0·19 | 0·0077 | 0·0077 |

hydrogen imparts to salts of bichromic acid a perchromate seems to be formed and is insoluble in ether. The existence of that colour is a convenient indication in this process of the peroxide of hydrogen which has escaped decomposition during titration, and unless that quantity is such as to render the colour of the liquid practically opaque about the completion of the operation, a further addition of that reagent will be necessary.

The peroxide of hydrogen I employed contained traces of acid, but too minute to be of consequence.

In manipulating the above process there is a tendency to overdo the addition of the acid, but the depth of colour imparted to the ether will roughly measure such an excess and be a guide to a more cautious titration in a second experiment. We may, alternatively, discharge the blue colour with standard chromate of potash solution.

The experimental results I append in examination of the process are carefully calculated from the grain to the grm. system of weights and measures ; I think the table will explain itself.

I have simply now to say that the acidimetric process for determining chromate is quick and easy of execution.

Laboratory of Clyde Iron Works (by Tolcross), Glasgow, December 20, 1886.

## THE RECIPROCAL RELATIONS BETWEEN THE PRINCIPAL FORCES OF NATURE.*

By M. EMILE SCHWŒRER.

In the monthly review, *Natur und Leben*, M. H. J. Klein, the well-known astronomer of Cologne, gave a remarkable analysis of two recent works, the one by M. Hein and the other by M. Clausius, concerning the reciprocal relations of the principal forces of nature. This analysis seems to me to be quite worthy of reproduction ; I have therefore the honour of laying it before the Academie des Sciences.

Starting with the statement made by M. Clausius, in his inaugural address as Rector of the University of Berne, and then examining attentively the more recent work published by M. Hirn under the title of "The Idea of Force," M. Klein shows very clearly that these two works constitute two characteristic steps in modern scientific philosophy.

M. Clausius points out, in a very complete manner, the difference which exists between the ideas formerly held by physicists concerning the forces of nature, such as heat, light, electricity, &c., and those which, through the recent progress of science, have since been substituted ; he dwells on the relations which exist between these different forces, but at the same time he lays stress on the strangely erroneous character of certain expressions which have been introduced ; he points out how incorrect are the terms *the transformation of heat into electricity*, and *electricity into heat*, &c. While examining these facts he gradually arrives at the formulation of the following important proposition, viz. :—That we can in all probability explain the propagation of radiant heat and light by the action of electric forces, and that we ought therefore to substitute electricity itself for the ancient *ether*, which is supposed to fill all space and all bodies.

According to M. Clausius the physical sciences have arrived at this fundamental point, that beyond ponderable matter there exists but one particular substance, and that all phenomena will be explained by the various movements of this substance.

Passing then to the examination of the "Idea of Force" M. Klein makes it evident that M. Hirn has made an immense step in advance by considering force, taken generally, as a class of elements specifically distinct from so-called ponderable matter, by establishing the fact that electricity, heat, &c., the old imponderables of physics, are, in a word, not particular species of matter, or vehicles of force, but actually *forces* forming a common class with gravitation, for instance.

We cannot give M. Klein too much praise for the courage he has shown as a public man in pronouncing such a decided opinion in a great struggle, whose final result will be to definitely discredit the ancient doctrine of Epicurus, admitted under other names as truth exclusive to our epoch, and for having brought into the domain of experimental physics the great and important questions which had been relegated by public opinion to the shades of metaphysics.

* Read before the Academie des Sciences, Oct. 11, 1886.

## ON THE DENSITY OF WEAK AQUEOUS SOLUTIONS OF CERTAIN SALTS.*

By J. G. McGREGOR, D.Sc.

The following experiments were made with two objects : (1) to determine whether or not there are solutions of the salts used, given volumes of which are less than the volumes at the same temperature of the water which they contain ; and (2) to find how the density of very weak solutions varies with their strength.

Prof. Ewing† and I had found, by two experimental methods, that sufficiently weak solutions of sulphate of copper contain amounts of water whose volumes if free would be greater than those of the solutions themselves ; and that anhydrous copper sulphate, added in small quantities to water, produces solutions of smaller bulk than the original water. We had also‡ found that certain

* *Trans. Roy. Soc. Canada.*
† *Trans. Roy. Soc. Edin.*, vol. xxvii. (1873), p. 51 ; *Reports Brit. Assoc.* (1877) ; *Trans. Roy. Soc. Canada*, vol. ii. (1884), sec. iii., p. 69.
‡ *Trans. Roy. Soc. Edin.*, vol. xxvii. (1873), p. 51.

somewhat rough density-measurements had indicated the same peculiarity in the case of zinc sulphate. It seemed desirable, therefore, to subject this salt to careful experiments, and to extend the investigation to other hydrated salts.

The data which we possess as to the variation of the density of solutions with their strength, do not generally extend to weaker solutions than those which contain 2 or 3 per cent of salt, and are insufficient to settle the question. I have therefore made observations in the case of zinc sulphate and other salts, which both determine the question of the possession of the peculiarity referred to above, and supply a portion of what has hitherto been lacking in our knowledge of the phenomena of their solution.

My apparatus consisted of four dilatometers, which were large glass bottles (commonly called Winchester quarts), with glass tubes fitted in their necks. The bottles had capacities of about 2600 c.c. The glass tubes were about 25 c.m. in length and 0·4 sq. c.m. in section, and were chosen so as to be as uniform in bore as possible. They were fitted to the bottles by means of india-rubber stoppers, and fitted so tightly that there could be no danger of any relative displacement of tube and bottle. The rubber stoppers were held fast to the bottle by wires. Their inner ends were hollowed conically, and the glass tubes started from the summits of the conical hollows, so that air-bubbles could easily be made to pass up the tubes. At their upper ends the tubes widened into funnels. Fine scratches on the tubes served as zero marks. The bottles stood in a large zinc bath up to their necks in water. The dilatometers were calibrated by being filled with distilled water of known temperature, from measuring vessels whose volumes were known. The one used in calibrating the tubes was so divided that changes in the volume of the water it contained could be read to 0·05 c.c. The water, with which the bottles were thus filled, had been freed from air under the receiver of an air-pump.

To test the tightness of the stoppers, the dilatometers were filled until the upper surfaces of the water were near the tops of the tubes. The stoppers were thus subjected to as great pressures as they would be during the experiments. After the bottles had taken the temperature of the bath, I observed the variation of the height of the water in the tubes from time to time, until I had satisfied myself that there was no leak,—a return to a formerly observed height in one bottle being accompanied in all cases by a similar return in the others.

I next satisfied myself that differences of temperature between the bottles, greater than any which could arise during the experiments through the dissolving of salt in some bottles and not in others, would vanish in less than the time that was to intervene between successive measurements.

As the dilatometers could not be kept at constant temperature, and as any change of volume of their contents must therefore be partially due to change of temperature, it was necessary to know the relative apparent thermal expansion of their contents. For this purpose, both at the outset when all the bottles contained water, and at intervals during the series of experiments when some of them contained solutions, the temperature of the bath was varied, and the heights of the water or solutions in the different tubes were observed when the bottles had assumed the temperature of the bath. These results were tabulated for purposes of correction.

The solutions, whose volumes were measured, were formed by the addition of known masses of anhydrous salt to the water in the bottles. The salt was simply dropped little by little down the tubes of the dilatometers. In some cases no difficulty was experienced; in others the salt was found to cake occasionally at the surface of the liquid. In these cases various expedients were adopted to hasten the solution; but the greatest care was taken to prevent the loss, either of any of the salt which had been weighed out for solution, or of any of the liquid in the bottles. When the desired amount of salt had been added to a bottle, the upper end of the tube was closed with a small cork to prevent evaporation, and the bottle was put in the bath. After an interval of about twenty-two hours the bottle was taken out, and, if the salt was found to be dissolved, was first well corked and then rolled, until its contents had been thoroughly mixed. It was then replaced in the bath and left for another hour, when the height of the free surface of the liquid was observed. Not possessing a cathetometer, I required, for measuring differences of level, to trust to a steel scale placed in contact with the tube. Care was of course taken to avoid parallactic errors as much as possible.

To one of the four bottles no salt was added; and it was kept carefully corked up, so that the quantity of water it contained might be constant. The variation of the height of the water in the tube of this bottle was due, of course, to change of temperature alone. This variation being observed, and the relative apparent thermal expansions of the liquids in the four bottles being known from the subsidiary experiments referred to above, the variations, due to changes of temperature, of the heights of the solutions in the tubes of their respective bottles could be determined and eliminated. The variations of temperature were in all cases slight, the bath being large and its daily thermal history being very constant.

The salts which I used, zinc sulphate ($ZnSO_4$) magnesium sulphate ($MgSO_4$), and calcium chloride ($CaCl_2$) were bought as pure, repurified by crystallisation, and dehydrated by careful heating to the necessary temperature.

In all cases, after the solutions had stood a while, a slight fluffy appearance presented itself in the bottles. The mass of the precipitated solid was, however, very small,—so small that it was hardly possible to weigh it. Hence I considered that its effect on the result might be neglected. It was probably due to the presence of some impurity in the water, perhaps of ammmonia.

The following are the results of the experiments :—

*Zinc Sulphate*—$ZnSO_4$.

Volume of bottle to zero mark at 19·5° C. = 2687 c.c.
Mass of water in bottle = 2683·1 grms.
Mean section of tube = 0·40 sq. c.m.

| Mass of salt added. (Grms.) | Mass of salt per unit mass of water. | Mass of salt per unit mass of solution. | Rise of solution in tube, corrected for change of temperature. (c.m.) | Increment of volume per unit of initial volume. | Density of solution. (Grm. per c.c.) |
|---|---|---|---|---|---|
| 5 | 0·00186 | 0·00186 | 0·46 | 0·0000685 | 1·00179 |
| 5 | 0·00373 | 0·00371 | 1·10 | 0·0001638 | 1·00356 |
| 5 | 0·00559 | 0·00556 | 1·77 | 0·0002635 | 1·00530 |
| 5 | 0·00745 | 0·00740 | 2·24 | 0·0003335 | 1·00711 |
| 10 | 0·01118 | 0·01106 | 3·48 | 0·0005181 | 1·01065 |
| 10 | 0·01491 | 0·01469 | 5·36 | 0·0007979 | 1·01410 |
| 10 | 0·01863 | 0·01829 | 7·23 | 0·0010763 | 1·01753 |
| 10 | 0·02236 | 0·02187 | 8·12 | 0·0012089 | 1·02112 |
| 10 | 0·02609 | 0·02542 | 9·97 | 0·0014842 | 1·02446 |
| 10 | 0·02981 | 0·02895 | 11·98 | 0·0017834 | 1·02798 |

In the above Table the first and fourth columns contain the results of observation; the others are calculated from these. The third column shows the solutions examined to have been of strengths varying from 0·186 to 2·895 per cent of salt in solution. The fourth and fifth columns shew that even the weakest solution formed has a volume greater than that of the water which it contains.

The former rough measurements, alluded to above, which seemed to show that weak solutions of this salt had volumes less than the volumes of the water they contained, were made with solutions, the weakest of which was of about 2·5 per cent strength. It appears, therefore, that zinc sulphate solutions do not exhibit this peculiarity.

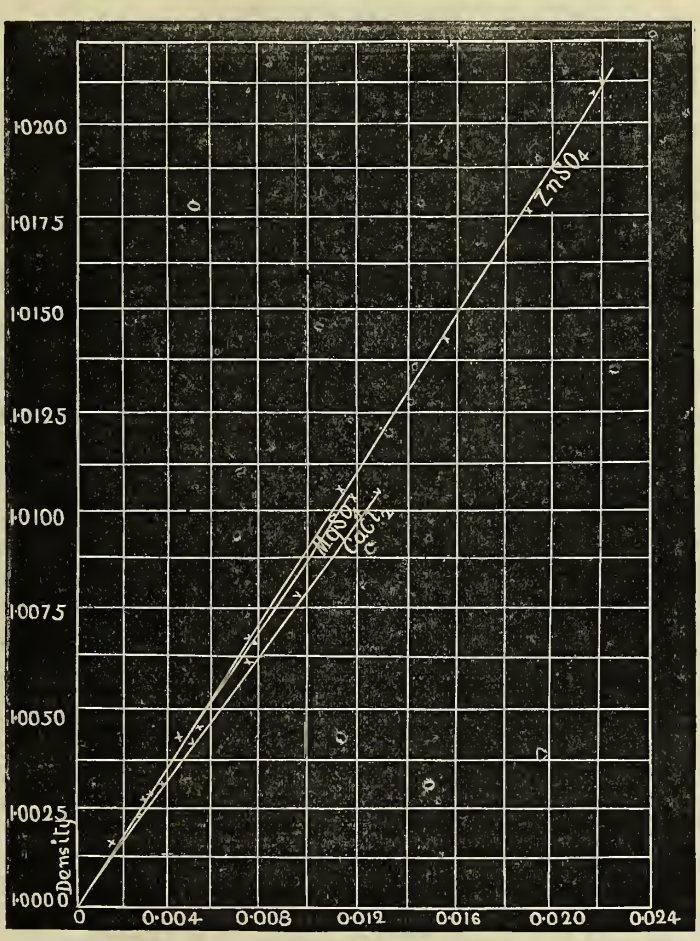
The relation between the mass of salt per unit mass of solution and the density of weak solutions of this salt is shown graphically in Plate I. The points determined by Schiff, is shown by the following numbers:—

According to Schiff, density = 1·0289 at 20°·5 C.
" Gerlach " = 1·0298 at 15°· C.
" above table " = 1·0280 at 19°·5 C.

This is the only one of the above solutions with which Schiff's and Gerlach's results are comparable. (See Table at top of next page).

As in the former table, the first and fourth columns contain the experimental results. The strengths of the solutions examined varied from 0·191 to 1·132 per cent of salt in solution. The fourth and fifth columns show that the volumes of all these solutions are greater than those of the water they contain. This salt therefore does not exhibit the same peculiarity as copper sulphate.

The relation between the concentration and the density




Mass of Anhydrous Salt in Unit Mass of Solution.

taking the former as abscissæ, the excess of the latter over unity as ordinates, are found to lie very nearly on a straight line passing through the origin. For these solutions, therefore, the increase of density, due to the addition of anhydrous salt to water, is approximately simply proportional to the percentage of salt in the solution thus formed.

The agreement of the density of the strongest solution of the above table with that of the same solution as determined by interpolation in the results of Gerlach* and of

* Gerlach, *Fresenius's Zeitschrift*, viii. (1869), 245.

of these solutions is shown graphically in Plate I. The points, whose co-ordinates are the mass of salt per unit mass of solution and the excess of the density over unity respectively, lie very nearly on a straight line passing through the origin. For weak solutions of this salt, therefore, the increase of density is simply proportional to the percentage of salt in solution.

So far as I know, there are no existing observations with which any of the above may be compared. Those of Hassenfratz, Schiff, and Gerlach were all made with solutions of greater strength. (See Table on next page).

The direct experimental results are contained in the

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*Magnesium Sulphate*—$MgSO_4$.

Volume of bottle to zero mark at 9·5° C. = 2619·6 c.c.
Mass of water in bottle = 2618·9 grms.
Mean section of tube = 0·40 sq. c.m.

| Mass of salt added. (Grms.) | Mass of salt per unit mass of water. | Mass of salt per unit mass of solution. | Rise of solution in tube, (corrected for variation of temp.) (C.m.) | Increment of volume per unit of initial volume. | Density of solution. (Grm. per c.c.) |
|---|---|---|---|---|---|
| 5 | 0·00191 | 0·00191 | 0·93 | 0·0001420 | 1·00170 |
| 5 | 0·00382 | 0·00380 | 2·25 | 0·0003436 | 1·00346 |
| 5 | 0·00573 | 0·00569 | 3·06 | 0·0004672 | 1·00526 |
| 5 | 0·00763 | 0·00758 | 3·80 | 0·0005802 | 1·00705 |
| 10 | 0·01145 | 0·01132 | 5·48 | 0·0008368 | 1·01060 |

*Calcium Chloride*—$CaCl_2$.

Volume of bottle to zero mark at 9·5° = 2616·5 c.c.
Mass of water in bottle = 2615·8 grms.
Mean section of tube = 0·41 sq. c.m.

| Mass of salt added. (Grms.) | Mass of salt per unit mass of water. | Mass of salt per unit mass of solution. | Rise of solution in tube, (corrected for variation of temp.) (C.m.) | Increment of volume per unit of initial volume. | Density of solution. (Grm. per c.c ) |
|---|---|---|---|---|---|
| 5 | 0·00191 | 0·00191 | 1·57 | 0·0002478 | 1·00168 |
| 5 | 0·00382 | 0·00381 | 4·07 | 0·0006426 | 1·00317 |
| 5 | 0·00573 | 0·00570 | 6·67 | 0·0010528 | 1·00465 |
| 5 | 0·00765 | 0·00759 | 9·47 | 0·0014948 | 1·00615 |
| 5 | 0·00956 | 0·00947 | 12·19 | 0·0019241 | 1·00765 |
| 10 | 0·01338 | 0·01320 | 18·22 | 0·0028759 | 1·01050 |

first and fourth columns. The strengths of the solutions examined varied from 0·191 to 1·32 per cent of salt in solution. The fourth and fifth columns show that, as in the case of the other two salts examined, all the solutions were more bulky than the constituent water.

The relation between the concentration and the density of these solutions is shown graphically in Plate I., the mass of salt per unit mass of water being plotted against density. The result is a curve bending towards the axis of concentrations. In the case of this salt, therefore, the rate of change of density with concentration diminishes with the concentration.

I am not aware of the existence of any observations with which the above may be compared. Those of Schiff, Kremers, and Gerlach were all made with solutions of greater strength.

## ANALYSES OF COMMERCIAL FERTILISERS.*

(Continued from p. 329.)

The Secretary, in the absence of Dr. Dabney, read the following:—

Raleigh, N. C., August 24, 1886.

Gentlemen,—Your Committee on Nitrogen esteemed it most important to settle upon a general method for determining nitrogen in the course of fertiliser work. To this end they thought that the best plan was to send out a well-defined method along with the samples, which was to be used by all of the analysts, and compared with such other methods as they choose to try.

It was desirable that the method thus put on trial should be applicable to all the ordinary sources of nitrogen, simple, easy, and rapid of execution in the most ordinary laboratory, and that it should promise to give results agreeing fairly with those obtained by the so-called absolute method, when carried out with the best apparatus and manipulation.

The committee selected the Ruffle method as promising the most by this standard, and sent out a description of it to your members.

The results on the first samples were so late coming in that we were unable to send out other samples and another method, as we expected to do.

We have the honour of submitting herewith the results obtained by the Ruffle method, as described, and by some other methods, upon four samples of different kinds.

These results are encouraging. Omitting two or three very out of the way results, which are clearly due to accidents, the figures agree very well. The Committee's Ruffle method gives results on the different materials which agree remarkably well.

Your Committee suggests, therefore, the adoption of the Ruffle method, on trial, for general fertiliser work for one year. You will in this case, we hope, prepare detailed directions for carrying out the said method.—Respectfully submitted,

Committee:—
Charles W. Dabney, Jr., Chairman.
W. E. Moses.
John A. Myers.

To the Official Agricultural Chemists' Association.

*Results of the Determinations of Nitrogen in the Samples sent out by the Nitrogen Committee.*

(1) An ordinary ammoniated superphosphate of the trade.

(2) An ordinary ammoniated superphosphate of the trade.

(3) Cotton-seed meal.

(4) Three parts sugar c.p. to 1 part nitre c.p. calculated 3·47 per cent nitrogen or 3·38 nitrogen by the absolute method.

*The Ruffle Method for Nitrogen, as proposed by the Committee.*

*Reagents.*—

(1) Standard sol. $H_2SO_4$. 0·019968 grms. $SO_3$ to 1 c.c. Everything depends on the correctness of this solution.

(2) Standard sol. KOH of exactly same strength as the acid.

(3) Soda-lime crushed so that one-half is powder and one-half in granules.

(4) Hyposulphite soda coml. fused, almost water free and powdered.

(5) Charcoal and sulphur, equal parts by weight of flowers of sulphur and finely powdered wood charcoal (N-free).

(6) Saturated sol. of "coralline" in alcohol.

* From the *Proceedings* of the Third Annual Convention of the Association of Official Agricultural Chemists, at Washington, D.C. August 26 and 27, 1886. Edited by Clifford Richardson, Secretary.

Results Expressed as Nitrogen.

*By the Committee's Ruffle Method.*

| Analyst. | A. | B. | C. | D. | E. | F. | G. | H. | I. |
|---|---|---|---|---|---|---|---|---|---|
| 1 .. .. | 1·78 | 1·85 | 1·66 | 2·10 | — | 1·66 | 1·93 | 1·80 | 1·69 |
| 2 .. .. | 2·04 | 2·15 | 2·00 | 1·99 | — | 2·07 | 1·80 | 2·12 | 1·92 |
| 3 .. .. | 7·45 | 7·53 | 7·43 | 7·56 | — | 7·48 | 7·05 | 6·35 | 7·50 |
| 4 .. .. | 3·36 | 3·40 | 3·30 | 2·45 | 3·37 | 3·49 | 3·45 | 3·44 | 3·05 |

*By the Kjeldahl Method.*

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1 .. .. | — | 1·85 | — | 2·04 | — | 1·79 | — | — | — |
| 2 .. .. | — | 2·17 | — | 2·01 | — | 1·99 | — | — | — |
| 3 .. .. | — | 7·33 | — | 7·44 | — | 7·40 | — | — | — |
| 4 .. .. | — | — | — | — | — | *2·38 | — | — | — |

*By the Soda-Lime Method.*

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1 .. .. | 1·84 | 1·68 | — | 1·84 | — | 1·43 | — | — | — |
| 2 .. .. | 2·05 | 1·96 | — | 1·95 | — | 1·54 | — | — | — |
| 3 .. .. | 7·25 | 7·37 | 7·58 | 7·37 | — | 6·38 | — | — | — |
| 4 .. .. | 2·10 | — | — | — | — | 2·40 | — | — | — |

*Apparatus.*—

(1) Combustion furnace.

(2) U tube with stopcock.

(3) Two gallon bottles with syphon to aspirate.

(4) Combustion tube of best Bohemian glass, drawn to point, length 17½ inches; outside diameter ⅝ inch, inside diameter ½ inch.

*Preparation.*—

(1) Clean and fill U tube with 10 c.c. of $SO_3$ solution (or in proportion to the N expected).

(2) Fit cork and glass connecting tube (3), taking two sheets of letter-size paper No. 1 and No. 2; place on No. 1 two grms. powdered hypo., on No. 2 equal portions of soda lime and hypo., and mix. This mixture should be enough to fill 9 inches of the tube or about 15 to 20 grms. of each ingredient. Fill the tube as follows:—

(1) A plug of asbestos.

(2) One to one and a-half inches of hypo. and soda lime mixture from No. 2 paper.

(3) Mix intimately 1·4 grms. (or 0·7 or 2·8 grms., as is thought best) of the substance to be analysed with the powdered hypo. on No. 1; then add to the same 2 grms. of the C. and S. mixture; mix these thoroughly; next pour on No. 1 the mixture from No. 2, except enough to fill 1¼ inches of the tube; then mix carefully the mass now on No. 1 and pour into the tube; rinse off paper No. 1 with balance of hypo. and soda lime from No. 2.

(4) Knock down the contents of the tube as far as they will go; then further rinse off No. 1 with pure soda lime, and pour into the tube to within 1½ inch of the end (space for swelling of the mass).

(5) Another plug of asbestos and cork.

(6) Holding the filled tube nearly horizontal, tap on table until there is a gas channel all along the top of tube as it will lie in furnace. Place in furnace and make connections. Aspirate and see that all is tight.

*The Combustion*—

Commence by heating the pure soda lime portion until it is a good red heat; then turn up slowly jet after jet toward the other end of the tube, so that the bubbles come off two or three a second. When the whole tube is red hot and all bubbles cease and the liquid in the U tube begins to recede towards the furnace, lower the flames somewhat, break off end of tube, and aspirate to extent of about one-half litre. Detach U tube, wash contents into a beaker, add five drops coralline solution and titrate.

Follow this scheme closely on committee's samples, criticise it, and suggest changes.

(To be continued.)

* 2·76 with benzoic acid; 2·41 with sucrose.

## A METHOD FOR THE SEPARATION AND ESTIMATION OF BORIC ACID, WITH AN ACCOUNT OF A CONVENIENT FORM OF APPARATUS FOR QUANTITATIVE DISTILLATIONS.*

By F. A. GOOCH.

In all successful methods for the estimation of boric acid its comparative isolation is a necessary preliminary. Fortunately the removal of nearly everything which interferes seriously with the proper execution of methods is not particularly arduous, but, of ordinarily occurring substances, two, silica and alumina,—both very commonly associated with boric acid,—are especially annoying in this regard. In the separation of alumina the trouble lies in the tendency of the precipitated hydrate to carry and retain boric acid,† so that the two cannot be parted by means of ammonia or ammonia salts; with silica, the difficulty is in removing it completely. The volatility of boric acid stands, of course, absolutely in the way of treating with acid and evaporating to dryness, and every chemist knows the vainness of attempting to precipitate silica by means of ammonia, ammonia salts, or zinc oxide in ammonia. In Stromeyer's method‡ the presence of silica is peculiarly harmful, since in passing to the condition of potassium fluosilicate this substance nearly quadruples its weight, and to free the potassium fluo-borate from containing fluo-silicate requires, according to Fresenius,§ at least six treatments by solution in boiling water, the addition of ammonia, and evaporation to dryness. Wöhler ‖ recommends evaporating the hydrochloric acid solution to dryness in a flask fitted to a condenser, collecting the distillate, reuniting the latter with the residue, and filtering from silica; and the operation is successful so far as the complete removal of silica is concerned, but the alumina, if present, is still in condition to give annoyance, and the other bases are yet to be separated.

Advantage has long been taken of the volatility of free boric acid with hydrofluoric acid or with alcohol to secure its removal from fixed substances, but so far as I know no attempt has been made heretofore to secure its complete volatilisation and estimation in the distillate. The experiments which I proceed to describe are the result of an effort to accomplish this end.

Aside from the difficulties in manipulation and in the construction of apparatus which the use of hydrofluoric acid would involve, this reagent is otherwise plainly inapplicable to the purpose in view, and of other agents with which boric acid is known to volatilise freely methyl alcohol seems to present the most desirable qualities. Methyl alcohol, ethyl alcohol, and water are effective in the order in which they are named. Thus, to volatilise 1 grm. of boric acid,—the equivalent, speaking roughly, of about 0·5 grm. of boric anhydride,—two treatments with 10 c.m.³ of methyl alcohol and evaporation to dryness in each case were adequate; for the volatilisation of 0·2 grm. of boric acid were required two treatments of 10 c.m.³ each of ethyl alcohol, succeeding an evaporation with 50 c.m.³ of the same alcohol; and the residue of five evaporations of water over 0·4 grm. of boric acid, taking in each case 50 c.m.³ of water, followed by ignition, weighed 0·08 grm., or one-fifth of the original weight. In the presence of water, methyl alcohol is not equally effective; amyl alcohol and sulphuric acid restrain its action similarly, doubtless by dilution simply, and hydrochloric acid seems to possess no advantage over water alone in developing the volatility of boric acid. As an example, an experiment may serve in which a solution of 0·4 grm. of

* *Proceedings of the American Academy of Arts and Sciences* 18?6—87.

† Wöhler, *Ann. d. Chem. u. Pharm.*, cxli., 268.

‡ *Ann. d. Chem. u. Pharm.*, c., 82.

‖ "Quant. Chem. Anal.", p 424.

§ "Handbook of Mineral Analysis," under Datholite.

boric acid in 50 c.m.³ of water, after being heated three times successively with 25 c.m.³ of methyl alcohol until the boiling-point rose in every case nearly to that of water, and then evaporated to dryness, left a large residue which disappeared with a single charge of 25 c.m.³ of methyl alcohol applied by itself.

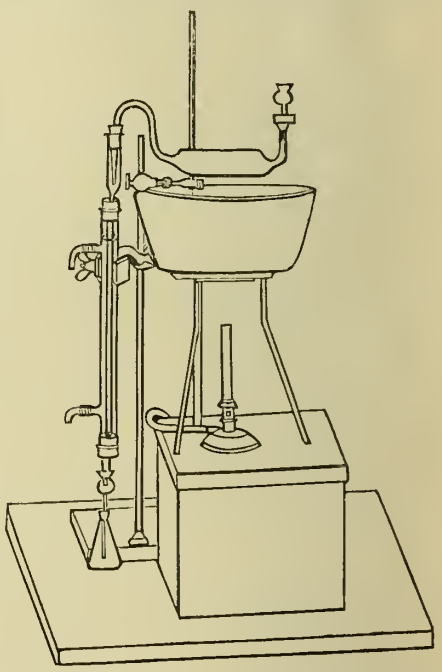
From the residue of the evaporation of borax with hydrochloric, nitric, or acetic acid, methyl alcohol, as would naturally be predicted, volatilises the boric acid freely, though the presence of foreign material acts to a certain degree protectively and tends to diminish the rapidity with which the alcohol would otherwise effect extraction and volatilisation. In case, however, that acetic acid is used to break up the borate, the tendency of sodic acetate to lose acid and become alkaline simply by exposure to evaporation in its aqueous solution makes it necessary to insure the acidity of the residue of evaporation by adding a drop or two of acetic acid before repeating the treatment with methyl alcohol.

On the whole, methyl alcohol shows itself to be an excellent agent by which to secure the volatilisation of boric acid.

To retain free boric acid, magnesium oxide naturally suggests itself. According to Marignac* it is effective, and, if in the course of analysis it may have been partly converted to the chloride, it is easily regenerated by the action of heat and moisture. Marignac, it will be remembered, makes use of magnesia mixture—the chlorides of ammonium and magnesium with free ammonia—to fix the boric acid, evaporating the solution to dryness, igniting, extracting with boiling water, filtering, and weighing the residue, while the filtrate is again treated as before to recover traces of the borate which have yielded to the solvent action of the water. During the drying and ignition the magnesium chloride yields hydrochloric acid, and it would seem scarcely possible that the magnesium borate should fail to show some loss of boric acid when both hydrochloric acid and moisture exert their action. Further, the presence of ammonia during evaporation does not prevent the volatilisation of boric acid,† and Marignac regards the addition of it from time to time as of doubtful use. So it appears natural to look for some loss under such conditions, and Marignac fully recognises the fact that the apparent accuracy of his method is due to the balancing of errors, the inclusion of foreign matter by the magnesium borate, and the deficiency of the magnesia when precipitated as ammonio-magnesium phosphate together compensating for the loss of boric acid by volatilisation. To bring the matter to the test, the following experiments were made. In them and in all succeeding experiments the boric acid was weighed in solution, the standard of this having been fixed by dissolving in a known weight of water a known weight of fused boric anhydride prepared in a state of purity by frequent recrystallisation. The magnesium oxide employed was made from the pure chloride by precipitating by ammonium carbonite and igniting, and was free from lime and alkalies, and as far as could be determined otherwise pure. The whole operation of each experiment was conducted in one vessel, so as to avoid transfers. In all cases a weighed platinum crucible of 100 c.m.³ capacity received a weighed portion of magnesia, and after ignition and subsequent weighing the weighed solution of boric acid was introduced. In experiments (1) to (4) the magnesia was thoroughly stirred in the solution of boric acid, the evaporation carried at once to dryness, and the crucible and residue ignited and weighed; in experiments (5) to (8), the magnesia was dissolved, after the addition of the boric acid, in hydrochloric acid sufficient in amount to prevent the precipitation of magnesium hydrate on the subsequent addition of ammonia, ammonia introduced in considerable excess in (7) and (8), in distinct excess in (5) and (6), the whole evaporated and ignited, the residue moistened and again ignited, and this last treatment repeated until the residue ceased to yield vapour of hydrochloric acid when heated.

| | $B_2O_3$ taken. Grm. | MgO taken. Grm. | $MgO+B_2O_3$ found. Grm. | $B_2O_3$ found. Grm. | Error. Grm. |
|---|---|---|---|---|---|
| (1) | 0·1734 | 0·5005 | 0·6607 | 0·1602 | 0·0132 – |
| (2) | 0·1804 | 0·4973 | 0·6660 | 0·1687 | 0·0117 – |
| (3) | 0·1793 | 0·4949 | 0·6640 | 0·1691 | 0·0102 – |
| (4) | 0·1794 | 0·4941 | 0·6627 | 0·1686 | 0·0108 – |
| (5) | 0·1807 | 0·4984 | 0·6542 | 0·1558 | 0·0249 – |
| (6) | 0·1789 | 0·4974 | 0·6687 | 0·1560 | 0·0229 – |
| (7) | 0·1806 | 0·4944 | 0·6684 | 0·1740 | 0·0066 – |
| (8) | 0·1789 | 0·4959 | 0·6672 | 0·1713 | 0·0076 – |

From these results it appears plain that under the conditions of the experiments neither magnesia alone nor the magnesia mixture is efficient in fixing boric acid; but in experiments (7) and (8), in which ammonia was employed in large excess, the loss of boric acid is least, so that it



would seem to be the case that though ammonia is not a perfect preventive of volatilisation it does exert a restraining action on the boric acid. That the magnesia mixture should be incapable of retaining entirely the boric acid present is, as has been pointed out, not surprising; but that the loss should be so great is rather startling, and more than suggests that the errors of Marignac's process are seriously excessive. The failure of magnesium oxide to hold back boric acid under the conditions of the experiment must be due to a cause other than that which determines the loss during the evaporation and ignition of the magnesia mixture, and for this it is natural to turn to the insolubility of the oxide—a quality likely to oppose some difficulty in the way of establishing complete contact between the boric acid and the magnesia during a short exposure. Direct tests of this point showed distinctly that mixtures of boric acid in water and magnesia, when submitted at once to distillation, yielded boric acid to the distillate; but that, if the mixtures were permitted to stand some hours before distilling, the oxide passed to the semi-gelatinous condition of the hydrate, and retained the boric acid so firmly that turmeric failed to show the

* *Zeit. fur Anal. Chem.*, i. 406
† Rose, *Pogg. Ann.*, lxxx., 262

presence of the latter in the distillate. It is plain, therefore, that with sufficient preliminary exposure magnesia might be relied upon to retain boric acid; but inasmuch as long and perhaps somewhat indefinite periods of waiting are objectionable in any analytical process, it was thought best to try the effect of substituting lime for magnesia. Experiments (9) to (12), conducted like the previous ones, excepting only the use of carefully prepared and ignited calcium oxide instead of magnesium oxide, were made with this end in view.

| | $B_2O_3$ taken. Grm. | CaO taken. Grm. | $CaO+B_2O_3$ found. Grm. | $B_2O$ found. Grm. | Error. Grm. |
|---|---|---|---|---|---|
| (9) | 0·1810 | 0·9737 | 1·1560 | 0·1823 | 0·0013+ |
| (10) | 0·1819 | 0·9750 | 1·1583 | 0·1833 | 0·0014+ |
| (11) | 0·1808 | 0·9922 | 1·1810 | 0·1818 | 0·0010+ |
| (12) | 0·1833 | 0·9715 | 1·1560 | 0·1845 | 0·0012+ |

These figures indicate sufficiently that there is no loss of boric acid by volatilisation when its aqueous solution is evaporated in contact with calcium hydrate; but, inasmuch as the comparative solubility of the latter is the quality which makes it effective where magnesia is not, it seemed desirable to test the action of calcium hydrate in alcoholic solutions, in which it is very insoluble. The experiment showed that when the solution of boric acid in methyl or ethyl alcohol is put upon lime and distilled at once loss is apt to take place, and sometimes to a very considerable amount, but that a short period of digestion with occasional stirring—from five to fifteen minutes—is sufficient to obviate danger of volatilisation of boric acid.

It appears, therefore, that free boric acid being easily volatilised by means of methyl alcohol and fixed completely by calcic hydrate, the separation of the acid from almost everything with which it occurs ordinarily and its estimation subsequently depend only upon the practicability of distilling it from its compounds in such company that it may be retained by lime and its amount determined by the increase in the weight of the latter. Unlike magnesium chloride, calcium chloride does not yield its chlorine readily under the action of heat and moisture naturally retained; so that hydrochloric acid must not be present with boric acid which is to be estimated in the manner described. Calcium nitrate and calcium acetate both yield the oxide without difficulty upon ignition, and nitric and acetic acids are suitable agents, therefore, for the liberation of boric acid previous to distillation.

The actual distillation presented at first some difficulty—for the repeated, thorough, and rapid evaporation of a liquid charged with soluble or insoluble solid matter is apt to involve some mechanical transfer to the distillate of material which should remain in the residue—but the device of the following description solves the problem successfully.

The apparatus, which is shown in the accompanying cut, consists essentially of a retort, condenser, and bath for heating. For the last I have used a paraffin bath, as being on the whole the most convenient. The condenser is set vertically, to facilitate changing the level of the retort within the bath, and to secure at the same time continual and thorough washing of the tube by its own condensations. The retort, somewhat like the well-known drying tube of Liebig in general shape, is easily made of a pipette by bending the tube at one end to a right angle, at the other to a goose-neck, as shown. To the former end is fitted, by a rubber stopper or section of tubing, a glass funnel-tube provided with a stop-cock; the end of the goose-neck passes tightly through a rubber stopper in the upper end of the condensing tube. This is essentially the apparatus, but it is convenient to attach to receive the distillate a small Erlenmeyer flask which moves with the condenser and is joined to it, in the manner indicated in the figure, by means of a thistle-tube and a rubber stopper grooved to permit the free passage of air. In carrying out a distillation, the liquid to be distilled is introduced into the retort either by the funnel-tube or previous to its insertion, the glass cock is closed, the water started through the condenser, and the retort lowered into the hot paraffin, care being taken to begin the operation with the retort not more than half full and so inclined that only the rear dips below the surface of the bath. If the precaution to heat the retort at the start in this manner be overlooked, it may sometimes happen that the sudden and violent expulsion of the air through the liquid will carry portions of it bodily into the goose-neck, and even into the condenser. With this point considered, the remainder of the operation presents no difficulty, and requires little care.

The size of the retort may be suited, of course, to the particular case in hand, but for most purposes a 200 c.m.³ pipette makes a retort of convenient dimensions, neither too large for the distillation of small charges nor too small to permit the treatment of 100 c.m.³ of liquid comfortably. The tube of the goose-neck should be wide enough to prevent the formation of bubbles in it; 0·7 c.m. is a good measure for the interior diameter. It is of advantage to heat the bath to a point considerably above the temperature at which the liquid which is to be distilled boils,—something between 130° C. and 140° C. does very well for water, and is not too high for methyl alcohol,—and under such circumstances, and when the retort is entirely submerged, it often happens that evaporation takes place with extreme rapidity from the surface of the liquid in perfect quiet without actual boiling.

With such an apparatus the following experiments were made. The boric acid was weighed, as before, in solution, and to bring the condition of the experiment to that of an actual analysis, 1 grm. of pure sodium hydrate was added in solution, nitric acid or acetic acid to acidity and a little more, and the whole was introduced into the retort and distilled to dryness.

In those experiments in which nitric acid was employed, the methyl alcohol was introduced upon the residue thus dried in six successive portions of 10 c.m.³ each, and distilled to dryness; but in order to break up the residue of sodium nitrate, which by its insolubility might effect to some extent the protection of the boric acid from the action of the alcohol, 2 c.m.³ of water were introduced and evaporated between the second and third, and again between the fourth and fifth distillations.

When acetic acid was made use of to free the boric acid, the six distillations with methyl alcohol were made as before; but, sodium acetate being soluble in methyl alcohol, the intermediate treatments with water were unnecessary. With the fourth portion of methyl alcohol a few drops of acetic acid were added to preserve the acidity of the residue, which, as has been pointed out, tends to become alkaline under the treatment.

The residues of both processes of treatment were found to be free from boric acid by the exceedingly delicate test with turmeric, care being taken in the series of experiments in which nitric acid was used to oxidise nitrites by means of bromine (expelling the latter before making the test), and in the acetic acid series to acidify with hydrochloric acid sufficiently to counteract the tendency of the acetate by itself to brown the turmeric on evaporation.

The lime to retain the boric acid in the distillate was ignited in the crucible in which the evaporation of the distillate was to be made subsequently, and then transferred to the receiving flask attached to the condenser, so that the boric acid might be fixed during the distillation. To prevent the caking of the lime by the action of the alcohol, it was slaked with a little water before the distillation was begun.

In experiments (13) to (16) nitric acid was employed, and in (17) to (20) acetic acid was used, with the precaution noted, to liberate the boric acid.

In experiments (13) to (16) the mean error amounts to 0·0012+ grm.; the experiments (17) to (20) the mean error is a little more than 0·0010+ grm. Throughout the entire series of experiments the tendency to yield

| | $B_2O_3$ taken. Grm. | CaO taken. Grm. | $B_2O_3$+CaO found. Grm. | $B_2O_3$ found. Grm. | Error. Grm. |
|---|---|---|---|---|---|
| (13) | 0·1738 | 0·9647 | 1·1392 | 0·1745 | 0·0007+ |
| (14) | 0·1806 | 0·9639 | 1·1456 | 0·1817 | 0·0011+ |
| (15) | 0·1779 | 0·9665 | 1·1450 | 0·1785 | 0·0006+ |
| (16) | 0·1824 | 0·9739 | 1·1587 | 0·1848 | 0·0024+ |
| (17) | 0·1806 | 1·4559 | 1·6371 | 0·1812 | 0·0006+ |
| (18) | 0·1812 | 0·9720 | 1·1543 | 0·1823 | 0·0011+ |
| (19) | 0·1788 | 0·9986 | 1·1781 | 0·1795 | 0·0007+ |
| (20) | 0·1813 | 0·9527 | 1·1358 | 0·1831 | 0·0018+ |

figures slightly larger than the truth is manifest, but the error is quite within legitimate limits. The greatest care was taken to secure similarity of conditions under which the crucible and lime were weighed before and after the evaporation and absorption of boric acid, and the weight after ignition was taken in every case after cooling over sulphuric acid during a definite period of ten minutes in order to eliminate as far as possible the effect of atmospheric condensation upon a large surface of platinum. Ignitions were always finished over the blast-lamp, and constancy of weights secured.

The results of both modes of treatment are, on the whole, satisfactory, and equally so.

In the presence of chlorides, it is of course impossible to employ nitric acid to free the boric acid. Oxalic, citric, and tartaric acids also liberate hydrochloric acid to a considerable extent from alkaline chlorides. It was found, however, that when acetic acid was distilled over sodium and potassium chlorides only traces of hydrochloric acid passed into the distillate, and experiments (21) to (23) were made to determine whether these amounts are sufficient to vitiate the separation of boric acid from alkaline chlorides by distillation in the presence of free acetic acid. The details of treatment were identical with those of experiments (17) to (20), excepting only the addition of 0·5 grm. of sodium chloride to each portion before distillation.

| | $B_2O_3$ taken. Grm. | CaO taken. Grm. | $B_2O_3$+CaO found. Grm. | $B_2O_3$ found. Grm. | Error. Grm. |
|---|---|---|---|---|---|
| (21) | 0·1834 | 0·9842 | 1·1675 | 0·1833 | 0·0001− |
| (22) | 0·1831 | 0·9755 | 1·1593 | 0·1838 | 0·0007+ |
| (23) | 0·1761 | 0·9740 | 1·1523 | 0·1783 | 0·0022+ |

The mean error of these results is about 0·0009+ grm. and it is plain that the presence of sodium chloride does not materially change the conditions of the experiment. There seems, therefore, to be no reason why boric acid may not be separated by distillation from alkaline chlorides in presence of free acetic acid; but it was found that the presence of any considerable amount of potassium acetate is disadvantageous. Sodium acetate to a reasonable amount does not interfere with the favourable progress of the separation; but potassium acetate appears to require a much higher temperature for the expulsion of its water, and longer distillation.

When, therefore, chlorides are present in the salts from which boric acid is to be removed by distillation, the choice is open between two methods: the distillation may be made directly with an excess of acetic acid; or the hydrochloric acid may be first removed by means of silver nitrate, and the distillation of the filtrate proceeded with at once, or after precipitation of the excess of silver salt by means of sodium hydrate or carbonate, care being being taken to acidify again sufficiently with nitric acid after the removal of the silver. Of these two modes of proceeding, I incline to the treatment with nitric acid and the removal of the chlorine by precipitation; and this method has been used with success by others as well as myself, for some months, in the analysis of waters carrying boric acid, and natural borates.

The process in either modification is fairly accurate and easily executed, and admits of very wide application. Insoluble compounds in which the boric acid is to be determined may be dissolved in nitric acid at once, or, if necessary, first fused with sodium carbonate; and, fortunately, nearly everything which is volatile in the subsequent treatment and capable of forming with lime compounds not easily decomposable by heat may be removed by known processes. The combination of fluorine, silica, and boric acid is perhaps most difficult to treat; but the precipitation and removal of the first as calcium fluoride from the aqueous solution of a fusion in alkaline carbonate may, it is believed, be effected with care, and the mode of procedure from that point is simple.

The number of distillations necessary depends, of course, upon the amount of boric acid treated. To remove 0·2 grm. of boric anhydride completely to the distillate, six charges of methyl alcohol, of 10 c.m.$^3$ each, proved, as we have seen, to be ample.

The apparatus by the aid of which the distillation processes which have been described were carried out has found useful application in a number of other processes. In the determination of free and albumenoid ammoniai in waters which can be boiled quietly with difficulty, in the methods of estimating hydrofluoric acid which involve the expulsion of silicon fluoride from a mixture of the fluoride with sulphuric acid and silica, in the separation of iodine from bromides and chlorides by distilling with ferric sulphate and sulphuric acid, and of bromine from chlorides by means of permanganic acid, it has proved of value, and will doubtless be found convenient in many analytical processes in which quantitative separations by the distillation of liquids liable to spatter or boil explosively are involved.

# PROCEEDINGS OF SOCIETIES.

## AUSTRALASIAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

On November 10th, 1886, a meeting of intercolonial delegates was held at the Royal Society's Rooms, Elizabeth Street, for the purpose of forming an Australasian Association for the Advancement of Science. The following delegates were present:—Victoria: Field Naturalists' Club of Victoria, the Rev. Dr. Woolls, F.L.S.; Geological Society of Australasia and Historical Society of Australasia, Mr. R. T. Litton, F.L.S.; Royal Society of Victoria, Mr. K. L. Murray; Victorian Institute of Surveyors, Messrs. W. J. Conder and W. H. Nash; Victorian Engineering Association, Professor Kernot, M.A., and Mr. K. L. Murray. Queensland: Geographical Society of Australasia, Queensland Branch, Mr. J. P. Thompson, M.A., C.E.; Royal Society of Queensland, Mr. Henry Tryon. Tasmania: Mr. James Barnard. New Zealand: Philosophical Institute of Canterbury, Mr. S. Herbert Cox, F.C.S., F.G.S. New South Wales: Linnæan Society of New South Wales, Professor Stephen, M.A.; Royal Society of New South Wales, Mr. H. C. Russell, B.A., F.R.S., Professor Liversidge, F.R.S., Mr. C. S. Wilkinson, F.G.S., F.L.S.; New South Wales Zoological Society, Dr. A. T. Holroyd, F.L.S.; Sydney Branch of the Geographical Society of Australasia, and Sir Edward Strickland, K.C.B., F.R.G.S. In the absence of Mr. C. Rolleston, C.M.G., President of the Royal Society, Mr. Russell was voted to the chair.

Professor Liversidge, in response to a request from the Chairman, explained that the object of the meeting was the formation of an Australasian Association for the Advancement of Science, and he supposed they had all received a circular setting that object forth. Their business was to frame conditional rules, and to appoint a date for the first meeting in 1888, that year having been partly fixed upon because it was the hundredth anniversary of this colony, and when this subject was proposed it

was thought there would be an exhibition here that year, and therefore a good time for the meeting of scientific men.

The Chairman said the first resolution had been put down on the business paper to be proposed by Mr. Rolleston, but he (the Chairman) was bound to move it in that gentleman's absence. It was one about which he thought there could not be much question. The resolution was,—"That an association of the scientific societies of Australasia be formed under the name of 'The Australasian Association for the Advancement of Science.'" There had been heretofore in these colonies a great want of united action, and many subjects which might have been taken up had not been. It was therefore desirable that they should, by every means in their power, form associations for the furtherance of investigation. There were many objects for investigation which men coming from the civilised world took the honour and credit of studying that might otherwise belong to this colony. The formation of the Association would be the means of stirring them up to do work which they had hitherto left undone.

Sir Edward Strickland seconded the motion, which was unanimously carried.

Profassor Stephen moved,—"That the rules of the British Association as printed shall be adopted by the Australasian Association for the Advancement of Science, and such other rules of the British Association be followed as may be necessary until the first meeting of the Australasian Association."

Mr. J. P. Thompson seconded the motion, which was carried unanimously.

Professor Kernot moved—"That the President, Hon. Secretaries, and Hon. Treasurer shall be elected annually by ballot from amongst the representatives of the colony in which the meeting is to be held. The first election of officers shall be held in Sydney in March, 1888." He said that the three bodies with which he had the honour of being connected in Victoria had all received the proposal for the formation of an Australasian Association for the Advancement of Science with the greatest heartiness. No one had any shadow of misgiving as to the thing being good, and the sooner it was done the better. He took that opportunity of assuring the scientific gentlemen present that the three bodies he represented gave this scheme of federation of the scientific societies their hearty adherence, and would be most happy in every possible way to assist at the meeting of the Association which he trusted would be held in 1888.

Mr. R. T. Litton seconded the motion.

After some conversation the motion was carried unanimously.

Mr. Cox moved—"That the first meeting of the Association be held in the first week in September, 1888."

Mr. Conder seconded the motion, which was carried unanimously.

Moved by Mr. Tryon and seconded by Mr. Murray, it was unanimously resolved that Professor Liversidge be appointed convener for the next meeting, and a hearty vote of thanks was accorded to that gentleman for the part he had taken towards the formation of the new Association, general satisfaction being manifested at the successful result of the meeting.

A vote of thanks to the Chairman terminated the meeting.

---

Dr. Divers, F.R.S.—The Queen has been pleased to give and grant unto Edward Divers, Esq., M.D., F.R.S., Principal and Professor of Chemistry at the Imperial College of Engineering, Tokio, Her Majesty's Royal license and authority that he may accept and wear the insignia of the Order of the Rising Sun of the Third Class, which His Majesty the Emperor of Japan has been pleased to confer upon him in recognition of his services while actually and entirely employed beyond Her Majesty's dominions in His Imperial Majesty's service.

## NOTICES OF BOOKS.

*Letts's Diaries for* 1887. Cassell and Co., Limited, London, Paris, New York, and Melbourne. 1886.

Letts's Diaries are so well known to, and appreciated by, the public in general, and have held the foremost position for so long, that it is almost superfluous to say anything more than that they are quite up to the usual standard of excellence. The "Universal Diary" is very convenient for office use, though hardly large enough for the laboratory; the diaries can, however, be obtained in all sizes, to suit every requirement.

## CORRESPONDENCE.

### THE ACTION OF FUMING SULPHURIC ACID ON ALPHA-NAPHTHYLAMINE.

*To the Editor of the Chemical News.*

Sir,—It may be interesting to many of your readers, and more especially those engaged in the chemical industries, to refer to a matter that has just come under my observation.

On glancing through the second edition of the well-known German work of Dr. G. Schultz, "On the Chemistry of Coal Tar," &c., a work acknowledged to be the best in any language on the subject with which it deals, I lighted on a passage of which I beg to subjoin a translation; this passage will be found at the foot of page 513 and top of page 514, with appended footnote on page 514, in the third part of the first volume of the work in question. "In the German Patent, No. 5411 of the Badische Anilin and Soda Fabrik, the preparation of sulphonic acids of *a*-naphthylamine difficult of solubility is referred to. This preparation is accomplished either by sulphonating the naphthylamine with fuming acid (1 part of naphthylamine with 3 parts of fuming sulphuric acid of 80 per cent!) (the note of admiration is Dr. Schultz's) at 70° to 80° C., or by reduction of the nitronaphthalene-sulphonic acid by means of iron, which sulphonic acid had been prepared from 1 part of nitronaphthalene, 2 parts of ordinary, and 1 part of fuming sulphuric acid of 80 per cent of anhydride." Dr. Schultz has appended a footnote to the statement as regards the use of the fuming sulphuric acid of 80 per cent strength (3 parts) to be used upon the *a*-naphthylamine (1 part) at 70° to 80° C.

This footnote, literally translated, runs as follows:—"Here is evidently a printer's error, for *a*-naphthylamine is completely destroyed by such an acid." Looking, however, at the English patent, "a communication" from the patentees abroad, I find literally the same description, "One part by weight of naphthylamine (which naphthylamine is not stated) is mixed with about three parts by weight of fuming sulphuric acid containing about 80 per cent of anhydrous sulphuric acid, and the mixture is heated at a temperature of about 70° to 80°," &c.—I am, &c.,

Watson Smith, F.C.S., F.I.C.,
Lecturer in Chemical Technology in the Victoria University, &c.

### NICKEL LABORATORY UTENSILS.

*To the Editor of the Chemical News.*

Sir,—I have been less fortunate than Mr. Wanklyn in my experience with nickel as a material for crucibles. Soon after I heard that such vessels could be obtained I bought a small crucible, price 2s. 6d., and made a few simple experiments with its lid. I find in my notes:—

Over a good Bunsen flame—

| | | |
|---|---|---|
| Weight of polished lid.. .. .. | 13·045 | grms. |
| ,, after ignition .. .. .. | 13·048 | ,, |
| ,, ,, further heating .. | 13·040 | ,, |
| ,, ,, ,, ,, .. | 12·978 | ,, |

A brownish film appeared on the lid, which thickened till almost black flakes were formed, which adhered but loosely to the metal underneath them, and were brushed off before weighing.

Suspecting that these flakes contained carbon, and that their formation was due to the contact of the nickel with that part of the flame containing unoxidised bodies, I removed the lid to the extreme tip of the Bunsen flame, when after it had remained there one hour it had gained 2 m.grs. and weighed 12·980 grms. It was again heated for one hour in the same position, and its weight remained constant.

Its behaviour with reagents was then tried.

(1.) Nitre—

| | | |
|---|---|---|
| Weight after 15 minutes fusion .. .. | 12·992 | |
| ,, ,, 30 ,, ,, .. .. | 13·042 | |

The surface was blistered and evidently oxidised, as shown by the considerable gain in weight, but the nitre contained no nickel.

(2.) Caustic potash—

| | | |
|---|---|---|
| Weight of lid after cleaning .. .. | 12·9725 | grms. |
| ,, ,, ,, 10 minutes fusion | 12·9723 | ,, |

No nickel was detected in the potash.

(3.) Potassium cyanide—

Weight after 10 minutes fusion.. 12·9226 grms.

The potassium cyanide contained nickel.

The crucible itself was afterwards heated in a gas muffle; it became covered with loosely adhering scales of a beautiful lustre, like polished black-lead, on the outer side, and of a rough texture and grey-green hue on the other.

According to the foregoing experiments the uses of nickel for chemical purposes are confined to—

(i.) Dry ignitions (*i.e.*, not fusions) in an oxidising flame, provided the heat be not too intense.

(ii.) Fusions with caustic alkalies.

From which may probably be deduced—

(iii.) Fusions with barium hydrate.

(iv.) Fusions with alkaline carbonates.

This is surely an ample field for it, and it is, as Mr. Wanklyn points out, worthy of the chemist's further attention; but its inability to stand high temperatures, especially in contact with a reducing flame, limits its employment considerably, and demands caution in dealing with it.

It is just possible that the crucible and lid which I used were not a fair sample, and that their behaviour was due to some peculiarity; the experience of others under like conditions would elucidate this point.—I am, &c.,

BERTRAM BLOUNT.

23, Queen Anne's Gate, S.W., Jan. 4, 1887.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Biedermann's Central Blatt für Agrikultar Chemie.*
Vol. xv., Part 7.

**Sulphuric Acid as a Manure.**—Professor Farsky.—The author caused the strongest acid to act upon earth, mixing it frequently, and applied this compost to a field, whilst other lots were mixed at once with stro g acid, and others again with dilute acid. The direct influence of sulphuric acid upon the soil was favourable, but the yield was higher the more dilute the acid. If the cost of the acid is taken into account the apparent advantage of this manuring disappears.

**On Lactina.**—Professor F. Fleischmann.—A Hamburg firm offer a vegetable food for young animals under the name of "lactina"—said to be a perfect substitute for their mother's milk. It contains the meal of a leguminous seed. It is less costly than milk, but far poorer in proteine, fat, and mineral salts.

**The Feeding Value of Sorghum.**—W. Fersman and Professor Farsky.—Not adapted for useful abstraction.

**Solution of Starch in Leaves.**—Leon Brasse.—The author has detected in leaves a kind of diastase, known as amylase, which converts starch into a reductive sugar. This result has been confirmed by Schimper. He has now undertaken a comparison between amylase and malt-diastase.

**The Formation of Starch Granules in Leaves from Sugars, Mannite, and Glycerine.**—Arthur Meyer.—This paper is botanical rather than chemical in its import.

**On a Quantitative Determination of the Chlorophyll Pigment in Leaves.**—A. Hansen.—The leaves were extracted for a short time at a boil, the colouring matter dissolved out in alcohol at 96 per cent, the solution saponified, dried, and weighed after the expulsion of the solvent. The yellow and the green chlorophyll were not separated. Five parts of chlorophyll are engaged in the formation of 25 parts of starch.

**Extirpation of the Root-Fungus (Dematophora Necatrix) in Vineyards.**—Professor L. Just.—Naphthalin is not capable of destroying this fungus or of keeping it from attacking healthy vines. Vine-props soaked with creosote are also useless, and are themselves overgrown with the fungus.

**Analytical Detection of so-called "Saccharine."**—H. Reischauer.—One hundred grms. of sugar are let stand for some hours in a closed vessel with 150 to 200 c.c. of ether, shaking frequently. If a sample of sugar has an alkaline reaction a strong aqueous solution is used instead of solid sugar; it is slightly acidified with phosphoric acid and then shaken out with ether. The ethereal solution is then drawn off with a syphon and filtered. In both cases the ether takes up a large part of the saccharine, which is obtained in the residue, after distilling off the ether, almost free from sugar. The presence of saccharine is best demonstrated by cautiously heating the residue in a platinum crucible with a mixture of 6 parts pure sodium carbonate and nitre, and finally igniting, not too strongly. Saccharine contains sulphur, which is thus completely converted into sulphuric acid.

*Moniteur Scientifique, Quesneville.*
3rd Series. Vol. xvi., October, 1886.

**The Purple of the Solar Spectrum, the Synthesis of Red and Colouration in General.**—M. Camille Kœchlin.—Already inserted.

**Patents concerning Colouring Matters, taken out in Berlin.**—M. No. 4257. Monnet & Co., of La Plaine, April 6th, 1886.—Production upon the fibre itself, of greys more or less inclining to a blue or a brown by the simultaneous oxidation of aromatic monamines and diamines.

D. No. 2505. A. Dahl, February 17th, 1886. Process for preparing the disulphonic acids of mono-, di-, or tribenzylrosaniline.

W. No. 4039. A. Wulsing, March 1st, 1886. Separation of paratoluidine from orthotoluidine.

C. No. 1727. L. Casella. April 5th, 1886.—Preparation of blue-black azo-colours.

B. No. 6665. Baden Aniline Works. April 19th, 1886.

Preparation of a new yellow colour, galloflavine, by means of gallic acid.

B. No. 6511. C. F. Bœhringer. February 22nd, 1886. Preparation of orthonitroamidoparametoxylbenzine.

**On the Infusion of Tea.**—W. M. Green.—From the CHEMICAL NEWS.

**The Deposits of the Delta of the Nile.**—Sir W. Dawson.—From *Nature*.

**Krakatoa.**—Mr. Johnston Lavis.—From *Nature*.

**Method of Filtration by means of Filters readily Soluble and Volatile.**—F. Gooch.—From the *American Chemical Journal*.

**Solubility of Barium Sulphate in Hydrobromic and Hydrochloric Acids.**—A Haslam. — From the CHEMICAL NEWS.

**Volumetric Method for the Determination of Alumina.**—Dr. J. Beyer.—From the CHEMICAL NEWS.

**Adulteration of Olive Oil.**—From the *Pharmaceutical Journal*.

**On Water of Crystallisation.**—W. Nicol, D.Sc.—From the CHEMICAL NEWS.

**The Proportion of Moisture which Sulphuric Acid leaves in Gases.**—E. W. Morley.—From the *American Journal of Science*.

**Valuation by Distillation of Acetic Acid in Liquids containing Organic Matters.**—H. W. Wiley.—From the CHEMICAL NEWS.

**Optical Properties of Malic and Tartaric Acids.**—Louis Bell.—From the *American Chemical Journal*.

**The Temperature of Dissociation with Reference to Pyrotechnical Questions.**—F. Siemens.—A lecture delivered before the Royal Institution.

**Formation and Decomposition of Nitrates and Nitrites in Artificial Solutions and in Spring and River Waters.**—J. H. Munro.—From the *Journal of the Chemical Society*.

**The Centenary of M. Chevreul.**—An account of the proceedings at the Museum, at the Hotel de Ville, and at the Odeon.

**Discussion on the Fortification of Wines before the Academy of Medicine.**—Continued from the September issue.

**Industrial Society of Mulhouse. Session of the Chemical Section July 14th, 1886.**—M. C. Kœchlin spoke of the formation of Schweinfurt green obtained by treating copper arsenite with acetic acid or copper acetate with arsenious acid or any salt of copper with an alkaline arsenite and then with acetic acid. Koechlin finds that by substituting formic acid for acetic acid we obtain a green fully as beautiful and bright. If only the half proportion of formic acid is taken there is obtained a pale blue which cannot be produced with acetic acid. Of all the elements arsenic is the one which can find the most varied applications in dyeing and printing whilst the dangers attending its use have been very much exaggerated. M. O. Scheurer announced that he had succeeded in superseding the use of alkaline arseniates in dunging puce mordants by the direct addition to the colour of phosphorous or hypophosphorous acids along with a salt of copper. He sent in a series of swatches which "confirm his assertions." Nevertheless the best swatch was one which had been treated with arsenious acid and copper chloride. M. Setlick, chemist at the Thann Chemical Works, sent in a paper on a process for determining the double antimony and potassium oxalate which has recently come into use for fixing tannin. Into the solution of this salt there is poured a standard solution of soda until a slight turbidity appears. The alkali employed shows the free oxalic acid present. Phenolphthaleine is then added, upon which antimony hydroxide has no action, and the liquid is titrated until an alkaline reaction appears, thus obtaining the quantity of antimony oxide. To determine the alkali a fresh portion is precipitated with ammonia, filtered, the liquid evaporated to dryness, ignited, and the alkaline carbonate thus obtained is titrated with normal acid. M. Prud'homme sent in a paper on some derivatives of β-amidoalizarine. On condensing β-amidoalizarine with phthalic anhydride, a new colouring matter is obtained which dyes a reddish-brown on aluminous mordants. M. Weingaertner sent in a synoptical table of the reactions of the principal artificial colouring matters.

**Immisch Thermometers.**—From *Nature*.

**Volumetric Determination of Sulphates without Standard Solutions.**—H. Quantin.—This paper will be inserted in full.

November, 1886.

**Patents Granted at Berlin relating to Tinctorial Substances.**—These include a process for obtaining red colouring matters by the combination of β-nepthylamine, β-sulphonic acid with the diazo-derivatives, by Leopold Casella and Co.; azo-colours depending on the previous patent, P.R. No. 28,753, by the Berlin Aniline Company; preparation of rich anthracenes from pitch containing anthracene, by Messrs. Remy and Ehrhardt; preparation of tetrachlorobromic or tetrachloriodic pyrols, by Kalle and Co.; preparation of napthylamine sulphonic acids and of substituted napthylamines, by the Berlin Aniline Co.; improvement in the preparation of auramines, by the Baden Aniline Co.; preparation of a blue-black azo-colour, by the Berlin Aniline Co.; preparation of a dry alizarin which can be easily re-converted into a paste, by Leverkus and Son; preparation of the salicylic ethers of the phenols and naphthols, by Prof. Nencke and Dr. von Heyden; preparation of napthaline trisulphonic acid, and its conversion into napthol-disulphonic acid.

**German Review.**—M. G. Serracin.—A series of extracts from the *Berichte der Deutschen Chem. Gesellschaft*.

**Petroleum and its Products.**—Boverton Redwood.—A paper read before the Society of Arts.

**A Method of Illustrating the Periodic Law.**—Prof. J. Emerson Reynolds, F.R.S.—From the CHEMICAL NEWS.

**On Pseudo-Morphine.**—M. O. Hesse.—From *Liebig's Annalen*, and already noticed.

## MEETINGS FOR THE WEEK.

MONDAY, 10th.—London Institution, 5.
—— Medical, 8.30.
TUESDAY, 11th.—Institution of Civil Engineers 8.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
WEDNESDAY, 12th—Geological, 8.
—— Microscopical, 8.
THURSDAY, 13th.—Royal, 4.30.
—— London Institution, 6.
—— Mathematical, 8.
—— Telegraph Engineers, 8.
FRIDAY, 14th.—Astronomical, 8.
—— Quekett Club, 8.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

**Test for Nitronaphthalin.**—Can anyone indicate a test for the above in heavy mineral oils, where it is used for de-blooming, and is present to the extent of 1 to 3 per cent?—O. B.

## TO CORRESPONDENTS.

*Works Chemist.*—The letters F.C.S. mean Fellow of the Chemical Society. Write to the Secretary of the Chemical Society, Burlington House, W.

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January 7, 1887.

THE CHEMICAL NEWS.

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## MODE OF DISTINGUISHING HORSEFLESH FROM BEEF.

By JAMES BELL, D.Sc., F.R.S.

It having been alleged, in connection with a suggestion for legislation, that it was impracticable to distinguish by any ordinary method of analysis between horseflesh and beef, the question was submitted to me for report as to how far the statement was founded on fact.

As the result of a careful search for information, I found that very little had been done in this country on the subject, but I succeeded in obtaining some useful information from Paris as to the nature of the evidence upon which the Inspector of Slaughter-houses there, relies for distinguishing horseflesh from beef.

The characters relied on are as follows :—

1. Horseflesh is reddish brown, more or less dark, according to the quality, and gradually becomes darker when exposed to the air.
2. It has an odour peculiar to itself.
3. It is soft and but slightly tenacious, and the finger sinks easily into it. On working up the fibres a little, they break up and become pulpy.
4. The muscular fibres are long and fine, and united by very compact cellular tissue.
5. In cooking, horseflesh hardens and becomes more dense and compact than beef.
6. Under the microscope the fibres and striations of the muscular tissue are finer than in the flesh of the ox.

In a "Treatise on the Inspection of Butcher's Meat," by Baillet, and published by Asselin, of Paris, there is a comparative table showing the distinctive physical and anatomical characters of the flesh of the ox, cow, and horse, and it may be useful to give the table, of which the following is a translation :—

| | Flesh of | | |
|---|---|---|---|
| | Ox. | Cow. | Horse. |
| Colour | Bright red. | Bright red. | Dark red. |
| Consistence | Firm, hard, often even tough. | Firm, but soon becomes tender and unctuous. | Firm, hard, tough. |
| Cut | Resistant and large grain. | Easy and fine grain. | Resistant, large grain. |
| | Not mottled. | Mottled. | Not mottled. |
| Odour | Fresh, only that of beef. | Fresh, aromatic. | Musk-like. |
| Fat | No covering fat. Interior fat white. | Covering fat white or yellowish. | No covering fat. Interior fat white and firm. |
| Articular surface. | Rosy white. | Deep rose. | |
| Anatomical constitution | Muscular bundles with fibres smooth, long, and united by conjunctive tissue, loose, easily penetrated by the fat. | Muscular bundles more compact, more resistant. Conjunctive tissue loose or compact, according to the quality. | Muscular fibres short, crowded in long and thin bundles. |

These characters, which are purely physical and anatomical, appeared to me likely to enable an experienced person to form, from a careful inspection of the meat, a fairly reliable opinion as to its origin.

With the aid, therefore, of the table and the characters described above, we examined a large number of specimens of horseflesh and beef, but we failed to observe such sharply defined differences in their respective characters as would enable us to positively identify and distinguish the former from the latter.

In these circumstances it became necessary to seek in other directions for evidence of a more positive kind, and attention was directed to the fats, a point which appears to have escaped the notice of previous experimentalists.

It was observed that the adipose tissue of the horse was of a softer and more oily nature than that of beef, and it was thought that in this difference there might be found a solution of the problem.

A series of experiments was first made with the adipose tissue collected from different parts of the horse-flesh, such as the round, flank, ribs, kidneys, and heart. The fat was cut up into small pieces and placed in a glass beaker, which was heated in a water-bath until the whole of the fat was melted. The melted fat was then poured off while hot, and its sp. gr. taken at 100° F.

The fat which was first experimented upon was that collected from the round, and it was found to have a sp. gr. of 908·8. Like experiments were made with the portions of fatty tissue collected from the other parts above named, and the specific gravities of the melted fats only varied from 908·6 to 908·7, the results thus practically agreeing with the specific gravity of the fat obtained from the round.

It next became necessary to determine whether the fat contained in the lean portion of the meat corresponded in specific gravity with that derived from the adipose tissue. For this purpose a portion of the horseflesh, which was freed from all fatty tissue, was cut into small pieces and stewed with water, the fat being removed from time to time as it collected on the surface. This fat, when dried and filtered, was found to have a sp. gr. of 908·4 at 100° F., being only four-tenths below the highest gravity of the fats obtained directly from the adipose tissue.

The melted horse-fat, at 70° F., formed a clear oil, and the amount of solid fat deposited at lower temperatures was comparatively small.

A series of similar experiments was next made with the adipose tissue of beef, and with portions of the beef from which the whole of the fatty tissue had been removed.

The beef fat was solid in each case at ordinary temperatures, and the melting-points varied from 110° to 116° F., and in these respects it essentially differed from the specimens of horse-fat. From the high melting-points of the beef-fat it was necessary to take the sp. temperature of 120° F., and for the purpose of co to calculate the theoretical gravity at 100° F. temperature the sp. gr. of the beef fat ranged fr to 904·0, so that there exists a considerable between the specific gravities of the two kinds o this difference affords a positive means of distin horseflesh from beef.

The fact of horse-fat being fluid at a temperature of 70° F. is an important characteristic, and this property alone is almost decisive, in itself, as to the meat being horse-flesh, and is, moreover, a test which could be applied by any intelligent person.

In the case of sausages, where there is a suspicion of their being made with horseflesh, the point may be similarly determined by extracting the fat from the meat, and ascertaining its specific gravity and melting-point.

It may be added that the fat of mutton differs from horse-fat to an even greater degree than that of beef, and that the determination of its specific gravity and melting-point are alike applicable.

The fat of horseflesh, like that of beef and mutton, is free from any of the soluble fatty acids.

As the subject possesses a general interest I shall not allow the question to drop, but intend to pursue the enquiry in its relation to the fat of other animals, and to the determination of the constituent parts of horse-fat.

## NOTE ON THE ACTION OF CARBONATE OF POTASH ON SOAP-BUBBLES.

By Dr. LEVOIR.

In experiments in educational physics a very firm froth is obtained when carbonate of potash, at about one-fifth, is present in the soap. For experiments after Plateau on molecular physics it is a good adjunct when fatty matter is to be carefully avoided.

## FARADAY'S, BUNSEN'S, AND GIFFARD'S PRINCIPLE IN THE CONSTRUCTION OF LAMPS.

By Dr. LEVOIR.

It gives me pleasure to select this title, firstly, with the object of paying tribute to the science and zeal of these three eminent physicists of the three prominent nations in Europe; secondly, because it affords me the opportunity of directing attention to the basis of the construction of gas-burning lamps of small price but great power.

Faraday demonstrated the usefulness of metallic gauze or texture; Bunsen explained and introduced his tube-lamps among chemists; and Giffard first pointed out the fertile principle in his feed-water injector for transporting fluids and gases by the velocity of effluxion of gases and steam.

In my lamps these three principles are in use together, and when burning make a noise resembling that made by some of the lamps of Mr. Fletcher in Warrington. His form of the outlet for the gas, and the leech-mouth form of Bunsen, is not very practical, because it creates a disturbance in the motion of the air-molecules which have to be mixed with the light gas.

In Bunsen's form of outlet for gas the inflowing air must change its direction perpendicularly, which seriously interferes with the mixing of the effluent gas with the
I take a conical form, with a very thin and sharp
By doing this Giffard's principle is used for
the coal-gas with the air. Two or more cones
tter in large lamps, which can be much lower than
dinary shape or model. It is understood that the
of the gas is a cone from the centre of whose base
d a cylindrical hole. The edge must be very sharp.
inary combustion-furnace lamps for elementary
s the gas-flames show luminosity because the gas
one side of the tube, and is only accidentally mixed with the air by outside currents or draughts of air. In that case the gas passes unmixed with air as a ribbon through the tube. If the tube is narrow the friction is so great that a sooty flame results. With a length of 2 inches, a width of 7-16ths of an inch is at least necessary for avoiding the passage of gas without mixture of air. With a slight obstruction in the tube the friction is so great that a kind of filtration occurs where the air is interfered with in its passage to the coal-gas.

Delft (Holland), December 26, 1886.

## NICKEL LABORATORY UTENSILS.

By THOMAS T. P. BRUCE WARREN.

Some time ago I had occasion to make an examination of samples of German and English nickel cubes, and also a sample of English grain nickel. I found that the English samples were strongly attracted by the magnet, whilst the German samples were not at all attracted by the same magnet.

The important deduction gained by this result was that certain metals were capable of destroying the magnetic property of nickel.

It is a well-known fact that German silver wire is so far devoid of magnetic influence that it is used extensively for electrical purposes, such as resistance coils. The metal incorporated with nickel when used for this purpose is copper. This alloy is so ductile that there is no difficulty in drawing it into very fine wire; its toughness, when recently drawn, allows of its being covered with silk or cotton, the only precaution necessary being to use no more strain than is necessary to hold the wire taut in the covering machine.

It is a notorious fact that fine wires become in time so brittle that they break by simply being coiled on an ordinary bobbin. In addition to this fact it was found that these wires vary so much in resistance, and were so unreliable for permanency in this respect, that it has been replaced by an alloy of platinum and silver.

It is singular that so visible and important a change in the nickel alloy should have been passed over without some explanation. I have not found wires of thicker gauge—say 16 to 20 B.W.G.—become brittle, and in the finer wires I have noted this brittleness set in after a few months, even when no electrical current has been sent through them.

When my attention was drawn to nickel dishes, crucibles, gauze and wire triangles, which are now easily procured, I obtained a supply from Messrs. Townson and Mercer.

I found no indication of magnetic attraction, and, thinking that pure nickel was neither malleable nor ductile, I thought it would be interesting to find out what metal was alloyed with it which would so modify its physical character.

I found that a very small proportion of tin was present, and a very small quantity of iron, the latter perhaps being simply an accidental impurity. From the fact that the crucibles became lighter in weight by careful heating, arsenic or some volatile metal was suspected of being present; but as my analysis was followed by a negative result, I thought it was not improbable that dissociation at a high temperature would explain the changes taking place.

The wire triangle supports and gauze became brittle and quite rotten after a short time. There was evidently a contraction in the wire used for the triangles. The crucibles were blackened on the outside, but if carefully heated, and simply wiped on cooling, the loss was very slight; but in a smoky flame the crucible exfoliated in a black flaky deposit, and rapidly lost weight. These crucibles, if imbedded in magnesia, do not undergo these changes.

For alkaline fusions these dishes and crucibles are, so far as my experience goes, superior to platinum; but for obtaining water residues where chloride magnesium is present, the residue will be slightly contaminated with the metal, due to the acid which is liberated.

In any operation in which an alkaline or neutral substance can be used, nickel dishes or crucibles are valuable appendages to the laboratory.

That the addition of a para-magnetic metal to a diamagnetic metal should render the same indifferent, magnetically, is easily conceived, and this fact is beginning to receive a value which its importance deserves.

I cannot conclude this article without asking what our own manufacturers are about, as to leave the manufacture of these nickel appliances to our continental friends?

On a future occasion I hope to give the actual analyses of these vessels, and also the analyses of the cubes and grain nickel referred to.

## ON THE OCCURRENCE OF SILVER IN VOLCANIC ASH FROM THE ERUPTION OF COTOPAXI OF JULY 22ND and 23RD, 1885.*

By J. W. MALLET, M.D., F.R.S., University of Virginia.

A FEW months ago I received from Señor Julian R. Santos, of Ecuador, formerly a pupil of mine in the laboratory of this University, a specimen of volcanic ash collected at his place of residence, Bahia de Caraguez, on the coast of the Pacific, about 120 miles nearly due west from Cotopaxi. This, the highest and among the most mighty of the active volcanoes of our globe, burst forth into eruption about 11.30 p.m. on the 22nd of July, 1885, and the ash began to fall at Bahia de Caraguez at 7 a.m. on the next day, the 23rd. It fell there to the depth of several inches, this fact alone indicating the discharge of an enormous amount of solid matter into the atmosphere, although Señor Santos wrote to me that the unsettled condition of the country, disturbed by revolutionary movements, prevented his making extended enquiries which might have ascertained the area covered by the fall of ashes.

The specimen sent me consisted of a very finely divided powder, mobile and soft to the touch, of light brownish-grey colour. Under the microscope it appeared to be made up of minute granules and spicules, in general with sharp, more or less splintery edges. These were for the most part colourless and transparent, or white and translucent; some were reddish, some dark bottle-green, some brown, some black and opaque. Most of those clear enough to freely transmit light showed brilliant colours in a field of polarised light. Quartz, two felspars (one white, and one pink or reddish), augite, magnetite (strongly attracted, and easily removed by the end of a magnetic needle), and thin scales of deep red specular iron oxide were easily distinguished.

The ash on being strongly heated before the blowpipe, or even in considerable quantity in a small platinum crucible over the blast-lamp, turned dark red-brown, and fused to a nearly black slag.

On being boiled in its original state with water it gave up 0·21 per cent of soluble matter. The solution gave very distinctly the reactions of chlorine, a sulphate, and sodium; in a less marked degree the reactions of potassium. On boiling with strong hydrochloric acid, 6·94 per cent was dissolved, in addition to that already extracted by water; the acid solution was deeply coloured by iron.

The specific gravity of the ash was found = 2·624 at 18° C. as compared with water at the same temperature.

An analysis of the material taken as a whole, *i.e.*, without any previous mechanical separation of its consistent minerals, and without previous digestion with water or acid, but dried at 100° C., gave the following results:—

| | |
|---|---|
| $SiO_2$ .. .. .. .. | 56·89 |
| $TiO_2$ .. .. .. .. | trace |
| $Al_2O_3$ .. .. .. .. | 19·72 |
| $Fe_2O_3$ .. .. .. .. | 4·06 |
| FeO .. .. .. .. | 3·65 |
| MnO .. .. .. .. | trace |
| MgO .. .. .. .. | 1·91 |
| CaO .. .. .. .. | 5·87 |
| $Na_2O$ .. .. .. .. | 5·14 |
| $K_2O$ .. .. .. .. | 1·96 |
| $Li_2O$ .. .. .. .. | trace |
| Ag .. .. .. .. .. | ,, |
| Cl .. .. .. .. .. | ,, |
| $SO_4$ .. .. .. .. | ,, |
| $PO_4$ .. .. .. .. | ,, |
| $H_2O$ .. .. .. .. | 0·62 |
| | 99·82 |

Silver was first noticed after fusing as usual with mixed sodium and potassium carbonates, and dissolving in excess of hydrochloric acid, on the addition of sulphuretted hydrogen to the solution, which had been freed from silica; the sulphur thrown down by ferric chloride present was observed to be distinctly brown, and on being filtered out and carefully burned off before the blowpipe it left a minute bead of metallic silver. All the reagents and vessels used were scrupulously examined, but the silver could not be traced to any of them. It was afterwards found that the metal could be obtained from the ash by furnace assay—fusion with pure lead carbonate, sodium carbonate, and a little cream of tartar, and cupellation of the lead button produced; and a comparative experiment was made, with negative result, using larger quantities of the same reagents, but omitting the volcanic ash.

It was ascertained that silver could be extracted from the ash by boiling it with a solution of ammonia, or of potassium cyanide, or of sodium thiosulphate, but the metal was not dissolved out in appreciable amount on boiling with nitric acid. Hence, as seems most probable, it was present in the ash as silver chloride. The fact of its being found in the solution in hydrochloric acid of the mass resulting from fusion with the alkaline carbonates is of course easily explained by the solvent action upon silver chloride of the chlorides of sodium and potassium, and (when such minute quantities are concerned) of hydrochloric acid itself.

The discovery of silver in the ash in question adds for the first time this metal to the list of elementary substances observed in the materials ejected from volcanoes, and the addition derives some special interest from the fact of the ash having come from the greatest of the volcanic vents of the great argentiferous chain of the Andes.

Lead, which was found by Señor Santos himself, when a student here in 1879, in a specimen of ash from the eruption of Cotopaxi of August 23rd, 1878,* was sought for in the ash now reported upon, but neither it nor any other heavy metal beside silver was detectable.

Several concordant experiments proved that the silver was present to the extent of about one part in 83,600 of the ash, or about two-fifths of a troy ounce per ton of 2240 pounds. Small as is this proportion, it must represent a very large quantity of silver ejected during the eruption, in view of the vast masses of volcanic ash which must have been spread over such area as is indicated by the fall at so distant a point as Bahia de Caraguez.

On Resorcinic Acetal.—M. Causse.—This compound has the empirical formula $C_{28}H_{14}O_8$, which answers to a mol. of aldehyd and 2 mols. of resorcine less a mol. of water. It forms crystals of a decided yellow colour, which disappears on drying. They are insoluble in water, ether, chloroform, and benzene, but soluble in alcohol, by which it is in part decomposed.—*Journ. de Pharm.*, Oct. 15.

* A Paper read before the Royal Society, Jan. 6, 1887.

* Chemical News, Oct. 17, 1879 (vol. xl., p. 186.)

## A METHOD FOR THE SEPARATION OF SODIUM AND POTASSIUM FROM LITHIUM BY THE ACTION OF AMYL ALCOHOL ON THE CHLORIDES,

### WITH SOME REFERENCE TO A SIMILAR SEPARATION OF THE SAME FROM MAGNESIUM AND CALCIUM.

By F. A. GOOCH.

FOR the quantitative separation of lithium from sodium and potassium, Mayer's method,* which is based upon the precipitation of lithium as the tribasic phosphate, and Rammelsberg's† mode of parting the chlorides by means of a mixture of anhydrous alcohol and ether in equal parts, have been available.

The method of Mayer grew out of the older process of Berzelius,‡ which consisted essentially in treating the solution of the alkaline salts with phosphoric acid and sodium carbonate in excess, evaporating to dryness, and extracting with cold water. The result of a single analysis of the product thus obtained was the testimony upon which Berzelius rested the belief and statement that the salt was a double phosphate of lithium and sodium, which left upon ignition sodium and lithium pyrophosphates in equal molecules; and on this Berzelius based his process for the estimation of lithium. Rammelsberg,§ however, showed later that it was a tribasic phosphate which was actually obtained, and from his experiments arrived at the conclusion that the proportion of soda and lithia were variable within wide limits, the amounts of the former varying in the special cases investigated from 7·84 per cent to 28·38 per cent; and the same thing in substance was reiterated subsequently‖ in an account of a repetition of the work suggested by the criticism of Mayer. Mayer,¶ however, was unable to prepare under any conditions the double phosphate of Rammelsberg, and obtained invariably, when the preparation had been washed with sufficient care, trilithium phosphate free from sodium; but the point was made, that the phosphate is apt to be contaminated with lithium carbonate when sodium carbonate is employed to bring about alkalinity. Mayer therefore modifies the method of Berzelius by substituting sodium hydrate for the carbonate; and, proceeding, evaporates to dryness, treats the dry mass with as much water as is needed to dissolve the soluble salts with the aid of heat, adds a drop or two of sodium hydrate if necessary to restore alkalinity, and then ammonia in volume equal to that of the water already added, sets aside at a gentle heat, filters only after twelve hours, and washes with a mixture of ammonia and water in equal parts. From the filtrate and first washings a small amount of the lithium phosphate is to be recovered by evaporation and the repetition of the former treatment. According to Mayer, the precipitation of the phosphate may be effected with equal completeness by boiling the solution, prepared as before, instead of evaporating it; but the objection to this mode of proceeding is the tendency of the liquid carrying the precipitate to bump explosively. Careful washing, somewhat prolonged, is essential to secure the complete removal of salts of sodium and potassium, and it is remarked that the purity of the precipitate is shown by its failure to cake when strongly ignited.

This is the mode of proceeding by which Mayer separates lithium from sodium and potassium, isolating it as presumably pure trilithium phosphate and weighing it as the anhydrous salt. In dealing with mixtures of the chlorides in which the proportion of the lithium salt is relatively small, the removal of the greater part of sodium and potassium chlorides by a preliminary treatment with absolute alcohol is recommended. The following table comprises the results of Mayer's test analyses of lithium carbonate in the first seven, of lithium sulphate in the last two, re-calculated with the use of the number 7—the figure now generally accepted—as the atomic weight of lithium:—

| $Li_3PO_4$ equivalent to Salt taken. | $Li_3PO_4$ found. | Error. |
|---|---|---|
| Grm. | Grm. | Grm. |
| 1·3586 | 1·3719 | 0·0133+ |
| 1·5172 | 1·5088 | 0·0084− |
| 0·7519 | 0·7580 | 0·0061+ |
| 0·9561 | 0·9510 | 0·0051− |
| 1·2651 | 1·2646 | 0·0005− |
| 1·2197 | 1·2230 | 0·0033+ |
| 0·8991 | 0·9018 | 0·0027+ |
| 1·1325 | 1·1236 | 0·0089− |
| 0·9715 | 0·9665 | 0·0050− |

Fresenius* found on examining the method that several repetitions of the treatment by evaporation and extraction were required to complete the recovery of all lithium phosphate, and advised that the operation be continued until residual lithium phosphate fails to appear. The results of Fresenius's experiments with lithium carbonate, re-calculated with the use of the number 7 as the atomic weight of lithium, are given in the table appended:—

| $Li_3PO_4$ equivalent to Salt taken. Grm. | | $Li_3PO_4$ found. Dried at 100° C. Grm. | Ignited. Grm. | Error. Grm. |
|---|---|---|---|---|
| 0·7443 | after two treatments .. | 0·7243 | — | 0·0200− |
| | after three .. | 0·7385 | — | 0·0058− |
| | after four .. | 0·7433 | — | 0·0010− |
| 0·9820 | | 0·9861 | — | 0·0041+ |
| | | — | 0·9826 | 0·0006+ |
| 1·6341 | | 1·6342 | — | 0·0001+ |
| | | — | 1·6305 | 0·0036− |

Thus it will be seen that in the nine experiments of Mayer the error ranges from 0·0133+ grm. to 0·0089− grm., and that of the determinations of Fresenius from 0·0001+ grm. to 0·0041+ grm. for the dried precipitate, and from 0·0006+ grm. to 0·0036− grm. for the ignited precipitate.

If the tendency of lithium carbonate to fall in company with the phosphate were not to assert itself during the evaporations of solutions of salts of lithium in presence of sodium hydrate and in contact with ordinary atmospheric air, it would surely be strange, and this point may be fairly set down as one of the weak ones of the method; but the gravest source of error, and that indicated most unmistakably throughout the whole history of the process,—which has been recounted at some length for the purpose of emphasising this very matter,—is the impossibility of preparing the lithium phosphate in anything like a condition of freedom from other alkaline phosphates without a careful and prolonged washing, which is sure to result in loss of the lithium salt by solution. When it is remembered that according to Mayer's determinations trilithium phosphate requires for solution only 2539 parts of water, or 3920 parts of a mixture of ammonia and water in equal proportions, it is plain that the success of the method depends upon the ability of the analyst to wash to a condition of purity, and without loss of that which it is the purpose of the process to save, a precipitate peculiarly prone to retain foreign matter and soluble in the washing mixture in the proportion of ten milligrms. to every 40 c.m.³ of the latter. Of course washings will never be entirely saturated, nor will the precipitate be as soluble at the beginning of the operation as at the end, when the precipitant no longer exerts an action which tends to lessen solubility; but in view of the difficulties which present themselves, it is sufficiently obvious that exact results obtained by Mayer's

* *Ann. d. Chem. u. Pharm.*, xcviii., 193.
† *Pogg. Ann.*, lxvi., 79.
‡ *Ibid.*, iv., 245.
§ *Loc. cit.*
‖ *Pogg. Ann.*, cii., 443.
¶ *Loc. cit.*

* *Zeit. für. Anal. Chem.*, i., 42.

process owe their apparent accuracy to a fortuitous balance of errors. The difference of 0·0222 grm. between the extremes of Mayer's experimental results should not be surprising; and, at the best, the process is tedious and not entirely trustworthy—facts of which its author was not unmindful.

In Rammelsberg's method of separating lithium chloride from the chlorides of sodium and potassium the sources of error are, in brief, the solubility of sodium chloride and potassium chloride in the ether-alcohol mixture, the influence which the presence of small amounts of water exerts upon the solubility of these same salts, the difficulty of bringing the chlorides to the anhydrous condition without decomposing the lithium chloride to a greater or less extent, and the mechanical difficulties of transferring the fused or crusted chlorides to a suitable receptacle for digestion and agitation in the solvent, and of extracting perfectly the soluble constituents of closely compacted matter. Of the last two items nothing need be said in explanation beyond simply noting them. The third is particularly important, inasmuch as the tendency of lithium chloride, first noted, I believe, by Mayer, to exchange chlorine for oxygen when ignited in presence of water, results in the formation of lithium hydrate or, in contact with products of combustion, lithium carbonate, both of which are insoluble in the mixture of ether and alcohol, and remain with the sodium and potassium chlorides. As to the effect of water in the mixture, an experiment of Mayer, in which it was found that 100 c.m.$^3$ of a mixture of alcohol of 96 per cent and ether of 98 per cent dissolved 0·1100 grm. of sodium chloride, is instructive. In regard to the solubility of the chlorides of sodium and potassium in the mixture of anhydrous ether and alcohol, Rammelsberg's statement, that from 0·9770 grm. of pure strongly-heated sodium chloride with an undetermined amount of lithium chloride the mixture extracted 0·0130 grm., is, unfortunately, meaningless in the absence of information concerning the amount of solvent employed. J. Lawrence Smith* found, in making an examination of this mixture, that 10 c.m.$^3$ of the anhydrous ether-alcohol mixture extracted from 0·5 grm. of sodium chloride 0·0005 grm., and from 0·5 grm. of potassium chloride 0·0003 grm. Smith's mode of applying the method is better than the original; for, by taking care not to heat the mixed salts above 100° C., the danger of decomposing the lithium chloride is diminished, and by treating the dried salts with the ether-alcohol mixture in the capsule in which it is heated and weighed (protecting it by a small inverted bell-glass) the disadvantage of the transfer is avoided, but the danger is incurred that the mixed salts may not be thoroughly dried by heat so gentle. With this modification Smith obtained results which are rearranged in the following statement, and which do not throw a very favourable light upon the method.†

| NaCl taken. | KCl taken. | LiCl taken. | Weight dissolved. | Error. |
|---|---|---|---|---|
| Grm. | Grm. | Grm. | Grm. | Grm. |
| 0·2000 | 0·2000 | 0·0080 | 0·0101 | 0·0021+ |
| 0·2000 | 0·2000 | 0·0884 | 0·0862 | 0·0022− |
| 0·2000 | 0·2000 | 0·8195 | 0·8341 | 0·0146+ |

It is obvious, therefore, that neither the method of Rammelsberg nor that of Mayer may justly claim to be what a good process should be, accurate and rapid; and in the dilemma many chemists have been inclined to accept, with Bunsen,* the inherent disadvantage of an indirect process, and, in a mixture of sodium and lithium chlorides, calculate the percentage of each from the known weight of the mixture and its contents contents in chlorine, and in the mixture of the three chlorides calculate the percentage of each from the known weight of the mixture and the determined contents in chlorine and potassium. Here again, however, as in Rammelsberg's process, the difficulty of bringing the chlorides to a definite condition for weighing without decomposing the lithium chloride is an obstacle; and in case potassium is to be separated from large amounts of lithium by precipitation as potassio-platinic chloride, the concurrent precipitation of a similar salt of lithium, to which Jenzsch† has directed attention, may be the occasion of inexactness. So, the intrinsic unsatisfactoriness of indirect methods quite aside, it appears that in following Bunsen we have by no means all that is to be desired in an analytical method.

In looking about for better means for the separation of lithium from sodium and potassium, certain preliminary experiments on the behaviour of the chlorides of these elements toward amyl alcohol gave very encouraging indications, and subsequent quantitative tests have borne out the hope that a successful method of separation might be based upon these relations.

In amyl alcohol the chlorides of sodium and potassium are highly insoluble, lithium chloride dissolves freely, and the attraction of amyl alcohol for water is so slight and its boiling-point so far above 100° C. that the latter may be expelled without difficulty by the aid of gentle heating.

When amyl alcohol is poured into a solution of lithium chloride in water the liquid forms two layers, the aqueous solution of the salts at the bottom and the amyl alcohol now carrying a little water above. With the application of heat, the water evaporates slowly, then boils, and, passing through the alcohol, escapes, until toward the end of the operation the residual lithium chloride collects in a viscous globule, and finally dissolves, with the exception of a slight incrustation. If now the alcohol is cooled and a drop of strong hydrochloric acid added and brought in contact with the deposit, and the boiling repeated, the solution is complete. This deposit I take to be lithium hydrate, resulting from the decomposition of the chloride by the protracted action of water at a temperature near its boiling-point. The small amount of water which is added in and with the hydrochloric acid seems to exert no unfavourable influence, but rather to be beneficial in hastening the solution of the residue by securing immediate and sufficient contact.

In hot amyl alcohol, lithium chloride appears to be a little more soluble than in the same reagent at ordinary temperatures, but the solubility under the latter condition only was determined. By boiling the solution until turbidity began to show, cooling, filtering, and then evaporating a known volume of the concentrated solution to dryness and weighing the residue after converting it to the sulphate, it was found that one part of lithium chloride was held dissolved in the cold in about fifteen parts of amyl alcohol, 10 c.m.$^3$ of the solution containing in the mean 0·66 grm. of the chloride.

(To be continued).

**Determination of Glucose by Means of Standard Solutions.**—Dr. Quinquand.—The author modifies Violette's liquid as follows. He takes, Violette's liquid 10 c.c., isinglass 6 centigrms. The liquid is diluted with distilled water to ¼ litre, heated to a boil, and let cool. The isinglass is prepared by heating 2½ grm. isinglass in 10 c.c. soap boiler's lye (!) and diluting to ¼ litre with distilled water, 1 c.c. corresponding to 1 centigrm. The liquid is standardised by means of a solution of glucose prepared according to Soxhlet's method.—*Journ. de Pharm.*, Nov. 15.

* *Am. Jour. Sci.* [2], xvi., 56.

† Dr. Smith's language in the description of these experiments is somewhat ambiguous, but it is believed that these figures represent the meaning intended. After the presentation of the data of the first experiment given here with the correction of an obvious typographical error, it is said of the second and third experiments that "a similar mixture containing 18·10 per cent of chloride of lithium furnished a residue of 17·65 per cent," and "a similar mixture containing 67·20 per cent of chloride of lithium gave a residue of 68·40." I have taken this to mean that in all three experiments 0·2 grm. of sodium chloride and 0·2 grm. of potassium chloride were employed with the different proportions of lithium chloride indicated for each experiment. At all events, if this is not the meaning of the language made use of, it is difficult to see a definite value in the experiments.

* *Ann. d. Chem. u. Pharm.*, cxxii., 348.

† *Pogg. Ann.*, civ., 102.

## ANALYSES OF COMMERCIAL FERTILISERS.*

(Continued from p. 7.)

The Secretary then read a paper by Mr. G. L. Spencer, on

*The Kjeldahl Method for the Determination of Nitrogen.*

This method for nitrogen determinations has attracted considerable attention since it was announced some three years ago. It is of special interest to agricultural chemists, affording as it does a rapid method for the determination of nitrogen in most of its combinations. It has even been claimed that the nitrogen of nitrates can be determined in this way. The results of a large number of analyses of pure nitrates made in this laboratory indicate that this claim is an extravagant one. This will be discussed further on.

The original method as described by Kjeldahl* has been considerably improved and its application extended by other chemists, notably by Wilfarth,† and later by Asboth.‡ As these modifications are published in detail in the journals referred to, it is not necessary to repeat them here. The following is an outline of the method which I adopted; it is essentially that of Asboth:—

Take from 0·25 to 1 grm. of the substance under examination. Introduce it into a flask (500 c.c.); add 0·5 to 1 grm. anhydrous sulphate of copper, 1 grm. of mercury, and finally 15 c.c. of the following mixture:—

100 grms. sulphuric acid,
50 grms. phosphoric anhydride.

* From the *Proceedings* of the Third Annual Convention of the Association of Official Agricultural Chemists, at Washington, D.C., August 26 and 27, 1886. Edited by Clifford Richardson, Secretary.

* *Zeit. Anal. Chem.*, 1883, p. 366.
† Wilfarth's method, *Chem. Centralblatt*, 1885, p. 17.
‡ Asboth's method, *Ibid.*, 1886, p. 161.

*Nitrogen Determinations by Kjeldahl's Method.*

| Substance. | Number. | Serial number. | Per cent of N. | Average. | Trescot's results. Soda-lime. Per cent of N. | Soda-lime. Average. | Ruffle. Per cent of N. | Average. |
|---|---|---|---|---|---|---|---|---|
| Milk | *a*1 | — | 0·543 | 0·543 | 0·459 | 0·459 | — | — |
| „ | *a*2 | — | 0·459 | 0·459 | 0·465 | 0·465 | — | — |
| „ | *a*3 | — | 0·448 | 0·448 | 0·426 | 0·426 | — | — |
| „ | *b*4 | — | 0·448 | 0·448 | 0·502 | 0·502 | — | — |
| „ | *b*5 | — | 0·498 | 0·498 | 0·409 | 0·409 | — | — |
| Mustard | *b*6 | 4511 | 6·08 | — | 5·98 | — | — | — |
| „ | *c*7 | 4511 | 6·38 | — | 5·98 | — | — | — |
| „ | *b*8 | 4511 | 6·27 | — | 5·98 | — | — | — |
| „ | *b*9 | 4511 | 6·19 | — | 5·98 | — | — | — |
| „ | *b*10 | 4511 | 6·33 | 6·25 | 5·98 | 5·98 | — | — |
| „ | *d*11 | 4542 | 4·20 | — | 4·05 | — | — | — |
| „ | *d*12 | 4542 | 4·48 | — | 4·05 | — | — | — |
| „ | *d*13 | 4542 | 4·26 | — | 4·05 | — | — | — |
| „ | *d*14 | 4542 | 4·26 | 4·30 | 4·05 | 4·05 | — | — |
| „ | *e*15 | 4542 | 4·83 | — | 4·05 | — | — | — |
| „ | *e*16 | 4542 | 4·84 | — | 4·05 | — | — | — |
| „ | *e*17 | 4542 | 4·79 | 4·82 | 4·05 | 4·05 | — | — |
| Fertiliser | *d*18 | 4447 | 7·73 | — | 6·77 | — | — | — |
| „ | *d*19 | 4447 | 7·70 | — | 6·77 | — | — | — |
| „ | *d*20 | 4447 | 7·64 | — | 6·77 | — | — | — |
| „ | *d*21 | 4447 | 7·78 | 7·71 | 6·77 | 6·77 | — | — |
| Pepper | *e*22 | 4537 | 2·10 | — | 1·79 | — | — | — |
| „ | *f*23 | 4537 | 2·07 | 2·09 | 1·79 | 1·79 | — | — |
| Cotton-seed meal | *f*24 | 4194 | 7·39 | — | 6·35 | — | — | — |
| „ | *f*25 | 4194 | 7·36 | 7·37 | 6·35 | 6·35 | — | — |
| Casein | *f*26 | — | 13·44 | — | 13·07 | — | — | — |
| „ | *f*27 | — | 13·55 | 13·49 | 13·11 | 13·09 | — | — |
| Gluten | *f*28 | — | 16·02 | — | 16·23 | — | — | — |
| „ | *f*29 | — | 15·90 | 15·96 | 16·16 | 16·19 | — | — |
| Fertiliser | *f*30* | 4450 | 1·79 | — | 1·46 | — | 1·68 | — |
| „ | *f*31 | 4450 | 1·79 | 1·79 | 1·40 | 1·43 | 1·62 | 1·65 |
| „ | *f*32* | 4451 | 2·02 | — | 1·51 | — | 2·07 | — |
| „ | *f*33 | 4451 | 1·96 | 1·99 | 1·57 | 1·54 | 2·07 | 2·07 |
| Cotton-seed meal | *f*34* | 4452 | 7·42 | — | 6·38 | — | 7·48 | — |
| „ | *f*35 | 4452 | 7·39 | 7·40 | 6·38 | 6·38 | 7·48 | 7·48 |
| Fertiliser | *f*36* | 4453 | 2·35 | — | 2·02 | — | 3·42 | — |
| „ | *f*37 | 4453 | 2·41 | 2·37 | 2·05 | — | 3·58 | — |
| „ | *g*38 | 4453 | 2·80 | — | 2·13 | — | 3·58 | — |
| „ | *g*39 | 4453 | 2·72 | 2·76 | 2·24 | — | — | — |
| „ | *h*40 | 4453 | 2·41 | 2·41 | 2·40 | 2·17 | — | 3·53 |

*a* One-half grm. $CuSO_4$; the water foamed badly.
*b* One-half grm. $CuSO_4$; 100 c.c. water + Zn foamed badly.
*c* As above, except in $CuSO_4$ + Zn.
*d* One-half grm. $CuSO_4$; 50 c.c. $H_2O$.
*e* One-half grm. $CuSO_4$; 50 c.c. $H_2O$; 1 gr. $HgK_2S$ to precipitate Hg.
*f* Same as *e*, except + Zn.
*g* Same as *f*, except + benzoic acid.
*h* Same as *f*, except + pure sucrose.
* Samples furnished by the Committee.

Heat at a temperature a little below the boiling-point of the mixture. Half an hour is usually long enough to continue the heat. After thorough decomposition the contents of the flask are cooled, 50* c.c. water are added, and the solution is again cooled: 120 c.c. of the following solution are added:—

| | |
|---|---|
| Rochelle salt .. .. .. | 350 grms. |
| Sodium hydrate .. .. .. | 300 ,, |
| Water .. .. .. .. .. | 1 litre. |

As soon as sufficient sulphide of potassium to precipitate the mercury and a small piece of zinc have been added, the mixture is ready for distillation. Distil over about 50 c.c. into a standard acid solution. Titrate as usual.

I find that the addition of zinc is necessary to prevent bumping. By passing the vapours through a bulb containing broken glass, all liability to error, from portions of the alkali being carried over with the liberated hydrogen, is obviated. I prefer to have the bulb at the end of the tube projecting into the distillation flask. This is essentially the plan recommended by Pfeiffer† and Lehmann. A number of blank experiments demonstrated that there is no error from this source when this device is employed.

The accompanying Table gives a record of the experiments and the results obtained.

An inspection of the table shows that the results obtained were more uniform when mercury was employed.

The following results were obtained with C. P. ammonium salts:—

| Substance. | Kjeldahl. | Will and Varrentrapp. | Theoretical. |
|---|---|---|---|
| Ammonium chloride.. | 26·432 | 26·210 | 26·168 |
| | 26·430 | 26·210 | 26·168 |
| | 26·580 | 26·210 | 26·168 |
| Ammonium oxalate .. | 19·570 | 19·710 | 19·718 |
| | 20·220 | 19·710 | 19·718 |
| | 20·220 | 19·710 | 19·718 |
| | 20·040 | — | 19·718 |

I cannot account for the high percentages obtained with these salts. The combustion with soda-lime gives results varying but little from theory.

In his paper‡ Dr. Asboth recommends the addition of benzoic acid to the decomposing mixture when nitrates are present. Kjeldahl does not claim that the method is applicable to nitrates.

I have made a number of experiments by the method as suggested by Dr. Asboth. The results given in the following Table show that with this modification the work was very unsatisfactory:—

| Substance. | Kjeldahl. | Ruffle. | Theoretical. |
|---|---|---|---|
| Pure nitrate of sodium, com'l | 9·24 | — | 16·47 |
| | 9·21 | 15·65 | 16·47 |
| | 13·33 | 16·16 | 16·47 |
| | 13·33 | — | 16·47 |
| | 10·47 | — | 16·47 |
| | 11·20 | — | 16·47 |
| | 10·53 | — | 13·47 |
| Pure nitrate of potassium .. | 13·00 | 13·55 | 13·84 |
| | 12·94 | 13·66 | 13·84 |
| | 11·89 | 14·00 | 13·84 |

The unsatisfactory results obtained by the Kjeldahl and Ruffle methods with nitrates led me to experiment upon a method to accurately and quickly determine the nitrogen of nitrates and other forms in the same substance.

Not having had time to make but very few experiments I shall only outline the method and results.

Make an ordinary nitric acid determination by Schulze's method as modified by Tiemans. (See Fresenius, *Quant. Anal.*, p. 473.) Instead of employing ferrous chloride, as directed, I use the sulphate, which answers equally as well and is more convenient.

Transfer the residue from the nitric acid analysis to schälchen and evaporate to dryness, or dry in the flask used for determining the nitric acid. The nitrogen in the residue is determined by the Kjeldahl method. The nitric acid analysis can easily be made in three-quarters of an hour.

A number of experiments made on mixtures of nitrates and cotton-seed meal, gluten, &c., gave nearly theoretical results. It is possible that with very volatile ammonium compounds there might be a loss of ammonia in the nitric acid determination.

At some future time I hope to continue these experiments, and determine the value of this combination of the two methods.

*Conclusion.*

The results obtained (except with nitrates), and the facility with which analysis can be made, recommended the Kjeldahl method to chemists for a large proportion of nitrogen work usually done in agricultural laboratories.

*References.* — *Chem. Centralblatt*, 1885, p. 17; *Ibid.*, 1886, p. 161; *Zeit. Anal. Chem.*, 1883, p. 366; *Bulletin Soc. Chemie*, vol. xliv., p. 623; Chemical News, vol. lii., p. 162; *Ibid.*, p. 220; *Chemikerzeitung*, 1885, p. 780; *Chem. Centralblatt*, 1885, p. 585.

(To be continued.)

* 100 c.c. in the original method.

† Bulletin No. 7, Division of Chemistry, U.S. Dept. of Agrl., p. 43.

‡ *Chem. Centralblatt*, 1886, p. 161,

# PROCEEDINGS OF SOCIETIES.

## RUSSIAN CHEMICAL SOCIETY.

*Session October* 3/15, 1885.

M. Poehl communicated a new method of determining arsenic, and explained his bacterioscopic researches on the waters of St. Petersburg and its district.

M. Solonina, in continuing his researches on the action of dilute acids upon allylic alcohol, has obtained propylenic glycol in the aqueous portion of the product.

M. Semenoff finds that even in an aqueous solution maleic acid is transformed into fumaric acid if heated to 100°—130°.

M. Latschinoff has isolated from normal ox-gall a monobasic acid analogous to cholic acid, which he proposes to name choleinic acid.

M. Lidoff sent in a paper on the determination of the active chlorine in chloride of lime by a novel method. This method is based on the decomposition of formic acid by calcium hypochlorite.

*Session November* 7/19, 1885.

M. Poehl made a communication on micro-chemical analysis in chemico-legal cases, and on the photographic reproduction of these microscopic preparations.

M. Rosenblatt sent in a quantitative method for the separation of nickel and cobalt from other metals simultaneously precipitated by ammonium hydrosulphate. Potassium thiocarbonate gives a deep brown solution with the salts of nickel, and with those of cobalt an olive-green solution. In concentrated solutions both nickel and cobalt thiocarbonates are precipitated. These thiocarbonates are not decomposed if heated to 75°, whilst iron, chromium, aluminium, manganese, and zinc thiocarbonates, yield under similar circumstances precipitates of sulphides (iron, manganese, zinc), or of hydroxides (aluminium and chromium). The filtrate is decomposed by acetic acid to precipitate nickel and cobalt sulphides, and these metals are determined electrolytically. For qualitative determination the same liquid containing

nickel and cobalt thiocarbonates is decomposed by hydrogen peroxide.

M. Alexeef sought to explain by a chemical action of glass all the phenomena in which M. D. Konovaloff admits a catalytic action of this body.

M. Rantzoff brought before the Society certain regularities manifested in the atomic weights.

M. P. Schulten sent in a communication on the preparation of magnesium and cadmium oxides in a crystalline state.

M. Wroblewski sent in a note on one of the isomeric xylidines.

M. Werner forwarded a continuation of his thermochemical researches in the aromatic series.

M. Mendeleeff presented remarks on the relations existing between chemical phenomena and phenomena of contact or catalysis.

*Session December* 5/17, 1885.

Mdlle. Davidoff proved that the ether formed by the action of ethylene bromide upon potassium succinate in presence of absolute alcohol is ethyl succinate.

M. P. Latschinoff has analysed the cholanic and bilianic acids.

M. Werner sent in thermic studies on bromo-substitutions in the aromatic series.

M. A. Sabaneeff discussed the action of sulphuric acid upon oleic acid.

M. V. Pospékoff gave an account of azocumene.

M. D. Konovaloff made a communication with reference to the mechanics of liquids, showing that, setting out from the law of Van der Waals, we may deduce the law of the expansion of liquids, discovered by M. Mendeleeff.

M. Koutcheroff expounded his researches on the metallic carbides of the acetylenic series and the metallo-ammoniacal compounds.

M. D. Mendeleeff communicated his results on the densities of solutions of sulphuric acid.

M. Alexeef gave the continuation of his researches on the vapour tensions of solutions of liquids in liquids.

*Session January* 9/21, 1886.

M. Kondakoff described products obtained on treating isopropylethylene with dry chlorine.

M. Setchenoff made a communication on the increase of the coefficients of absorption of carbonic acid by saline solutions.

M. Mendeleeff found that the thermic data of Prof. Thompson admit into the solutions $H_2SO_4$. $mH_2O$ two of the hydrates deduced from the densities of these solutions.

M. Rantzoff gave a continuation of his deductions on the regularities of the atomic weights of the elements. He sees here a proof of the unity of the matter of which our elements are composed.

M. Mendeleeff opposed this idea.

M. Alexeeff proposed to manufacture cellulose by treating chips of wood with a boiling mixture of sodium sulphite and carbonate. He also replied to the remarks of MM. Menschoutkine and Konovaloff on the catalytic action of glass.

*Session February* 6/18, 1886.

M. Poehl communicated the continuation of his bacterioscopic researches.

M. Przibytek had succeeded in passing from the dioxide $C_4H_6O_2$ to furfurane and thiophene.

M. Goloubeff made a commmunication on the benzene of naphtha tar.

M. Wroblewsky sent in some remarks on the regularities of the disposition of the halogens and of the groups $NO_2$ on the substitution of hydrogen in benzene and its homologues.

M. Chechoukoff explained the results of his researches on the action of hydriodic acid upon isobutylene.

M. Sorokine sent in a communication on the anilides of galactose and levulose.

Papers were further handed in on behalf of M. Matoussevitch on the quantity of albumenoid matter in different forage plants; by M. Sivoloboff on the dichlorhydrine of mannite; and of M. Alekhine on melezitose.

M. Schroeder described experiments on supersaturated solutions of sodium hyposulphite. The results appear confirmatory of Nicol's law.

M. Setchenoff continued the account of his researches on the absorption of carbonic acid by saline solutions.

*Session March* 1/19, 1886.

M. Menschoutkine gave a communication on the constant of rapidity of the action of isobutylic alcohol upon acetic anhydride.

M. Werner sent in an account of researches on the formation-heat of the isomeres in the benzenic series.

M. Konovaloff read a paper on the decomposition of the acetate of tertiary amylic alcohol by acids.

M. Wilson had studied the action of chlorine and bromine upon potassium platinocyanide.

## NOTICES OF BOOKS.

*Old and New Chemistry: Which is Fittest for Survival?* And other Essays in Chemical Philosophy. By S. E. PHILLIPS, F.C.S. London: Wertheimer, Lea, and Co.

THE author of this work gives, by way of a Preface, a letter of protest to the Council of the Chemical Society. He had applied, it seems, during November, 1885, for a grant in aid of research, specifying the objects in view as being the analysis of the indium and gallium alums, and the synthesis of uric acid. He had stated in his application that he should be equally well satisfied if the Council would appoint some competent chemist to execute the investigation. That the application was refused appears from the context.

It is further stated that in May, 1886, Mr. Phillips sent in a paper on the "Urethane Reaction," to be read before the Society. This also appears to have been declined. These cases, the author thinks, "tend to justify the authoritative allegation that modern chemists object to free inquiry."

The discussion of the relative merits of "old" and "new" chemistry is given in the form of three essays, entitled respectively "A Brief and Popular Picture of the Chemistry of Fact and Observation," "How the Recent Progress of Knowledge strongly Points in that Direction," and, lastly, "An Appeal to Results." We cannot help asking whether the differences between the so-called "old" and "new" chemistry are not ultimately doomed to fade into insignificance in face of a newer development? Probably neither of them, as we now have it, is fit for ultimate survival.

We next find papers on the urethane reaction, on the aldehyds, ketones, and lactones, and on an outline of the cyanogen compounds.

An appendix treats of "cyanamid genesis," and a second appendix gives a list of unpublished essays on chemical philosophy.

## CORRESPONDENCE.

### ON THE COMPOSITION OF HYDRATED SALTS.

*To the Editor of the Chemical News.*

SIR,—We much regret that M. Maumené should have received our remarks on this subject in a spirit of such bitterness; all the more do we regret it because we are not able to withdraw or modify any part of them, in spite

of his glowing panegyric of his own theory to which they are opposed.

Our point is a very simple one, and, if controvertible, can be controverted by experiment only. Most anhydrous salts, even after being subject to the finest powdering and sifted through the finest silk sieve,* and even after drying at 200°, retain a very appreciable amount of enclosed water, and that it therefore is impossible to imagine that hydrated salts, which in very few cases can be sifted so fine, and which can hardly ever be heated or subjected to any previous drying process, should be free from such contained water; that the analysis of a hydrated salt can give no reliable information as to the exact percentage of *combined* water in it.

M. Maumené, it is true, denies that sodium chloride retains any water at 200°, but admits that it does so at 100° ("a few thousandths": according to our determination 0·2 to 0·7 per cent = 0·03 $H_2O$): even if he be right on this point our argument remains unaffected.

M. Maumené states that, according to his analyses, alum contains 28·73 $H_2O$, and magnesium sulphate 6·67 $H_2O$. One of us has made some dozens of analyses of ordinary crystallised alum, and has found the water present to correspond with 24 $H_2O$, and with magnesium sulphate some scores of analyses gave results corresponding to 7$H_2O$ within the second decimal place in the percentage. These salts appear to resemble potassium nitrate in not retaining any enclosed water. Unfortunately we are not, at the present time of writing, within reach of M. Maumené's original work on these salts; but if he relied on the barium sulphate method, or even on a direct estimation of the water as ordinarily performed, it is quite intelligible to us how the error in his results would have arisen (see Pickering, *Chem. Soc. Trans.*, 1885, p. 100; 1886, pp. 16 and 268).

It certainly was not our intention to make any general attack on M. Maumené's theory; but we venture to maintain that, however "beautiful" it be, and however much M. Maumené may bewail the "indifference" of chemists towards it, the majority of us are not prepared to accept his dictum that "all possible compounds in all chemical reactions without exception" are composed of "weights (of elements) which are absolutely equal," and that $KO_{4}{\cdot}875$, $NaO_{2}{\cdot}875$, and $(BaO)_9(HO)_{76}{\cdot}5$ are correct formulæ.

If we might be permitted in all humility to make a suggestion, it would be that whatever truth there may be in M. Maumené's theory would find a readier acceptance amongst English chemists were it not advocated by such arguments as "What it is necessary to prove and explain is that KO forms with HO, $(KO)_9(HO)_{47}$, &c. These truths are proved by the General Theory, because all that results from a general law is proved":—and were it not forced down our throats in what must sound in our insular and prejudiced ears strangely like a *galli cantus*:—

"The Maumené theory is of such universal application that it embraces chemistry in its entirety, without any exception,—lighting it with such clear light that one must be most completely enveloped in the clouds of *routine* not to be enlightened by it."—We are, &c.,

Spencer Pickering.
P. G. Sanford.

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**Certain Novel Properties of, and on the Analysis of, Gaseous Phosphorus Pentafluoride.**—H. Moissan.—The author has decomposed this compound by means of the induction spark, taking care that the gas, the mercury, and the tube are absolutely dry. It is much more stable than the corresponding chlorine compound.—*Comptes Rendus*, Vol. ciii., No. 25.

* It is scarcely necessary to add that that the more coarsely sifted samples were examined as well as the finer ones, in order to ascertain the effect of the size of the particles, and not "to purposely cause mistakes."

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. ciii., No. 25, December 20, 1886.

**Phosphorescence of Alumina.**—Edmond Becquerel.—In a memoir recently presented by M. de Boisbaudran to the Academy (vol. ciii., p. 1107) it is asserted that very pure precipitated alumina, when excited by electric discharges in a vacuum, does not give a red light, which, however, can be made to appear by the addition of 1-10,000th oxide of chrome. The author of that memoir deduces from his observations that the characteristic red light is not derived from alumina, but is due to the presence of chrome. M. Becquerel, on repeating the experiment with some of the very same material, obtained an opposite result, in conformity with his former observations. Some fragments of this supposed pure alumina were fixed on a slip of mica with a little gum, placed in the phosphoroscope, and excited by means of the electric arc. They gave an emission of red light, but very feeble and less intense than the light emitted by alumina containing chromium mium oxide, and submitted to the same treatment. But if this pure alumina is ignited for fifteen minutes in a porcelain crucible placed in a gas-furnace fed with compressed air, it becomes as brilliantly luminous and red in the phosphoroscope as alumina containing chrome. In the phosphoroscope we can see bodies only if their luminous emission, after irradiation, has a certain duration measured by the speed of rotation of the discs of the apparatus, but as active bodies may emit, simultaneously, luminous rays, the durations of which are different and shorter than that measured by the rotation of the discs, we can perceive these rays only at the moment when the light acts upon the bodies, that is to say, according to the case, either by means of the ultra-violet light, or, as the author has shown for the first time (see *Annales de Chimie et de Physique*, 3rd series, vol. lv., p. 92), by the aid of electric discharges or effluves in a vacuum. In these latter conditions we have the luminous effects which have been named effects of fluorescence, and which differ from others merely by their duration. Hence the effects presented by bodies excited by these different means are not the same. Further, in case of the effluve the bodies may receive the influence of rays much more refrangible than those furnished by concentrated sunlight, or even by the electric arc, and perhaps these bodies may be also directly excited by the electric discharges themselves. The effluve in a vacuum excites bodies differently according to the degree of exhaustion, and one body may give no effect in an insufficient vacuum, whilst it is brilliant in one more perfect. Conversely another body may be more luminous in the first case than the second, though both are strongly excited in the phosphoroscope. It may happen that the effluve, acting upon mixtures, excites differently each substance contained in the mixture. The effects observed in the phosphoroscope are more simple, but cannot be obtained with all bodies; those observed in a vacuum by means of the effluve are much more complex, but on analysing the light emitted with the spectroscope we may deduce interesting conclusions as to the nature of the substances.

**Certain Arrangements for Realising Birefringent Photometers without Polarising the Light.**—A. Cornu.—This paper does not admit of useful abstraction.

**Wines and Brandies of Raspberries and Strawberries.**—Alph. Rommier.—The author recommends the use of the ellipsoidal ferment in the preparation of these wines and liqueurs.

**Relations of Efflorescence and Deliquescence of Salts with the Maximum Tension of Saturated Solutions.**—H. Lescœur.—The author gives his scales of deliquescence and of efflorescence respectively in the form of tables.

**Formation – Heat of Potassium [illegible]thylate and Ethylate.**—M. de Forcrand.—Not adapte[illegible]or abstraction.

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*Journal de Pharmacie et de Chemie.*
Fifth Series, Vol. xiv., No. 8, October 15, 1886.

**Detection of Peptones in Blood and Urine.**—M. Georges.—The author precipitates all the coagulable albumen by means of heat, treats the urine with acetic acid and potassium-mercury iodide, washes the precipitate formed on a filter with cold water charged with acetic acid in the same proportion as is the urine, washes again with the same acid at a boil, and collects the liquid separately. The clear liquid collected deposits a precipitate on cooling if it has dissolved traces of peptonic matter. By neutralising he obtains a solution in which the reaction of biuret may be tried.

**Determination of the Dry Extract of Wines.**—E. Bouilhon.—Already noticed.

**Therapeutic Use of Allyl Tri-bromide.**—Armand de Fleury.—A medical paper.

**Separation of Strychnine and Morphine from Fatty Matters.**—M. Focke.—The suspected matter is exhausted in heat with alcohol acidified with tartaric acid. The liquid when cold is filtered, and evaporated on the water-bath. The residue is taken up with ten times its weight of water, and the solution is mixed with an excess of baryta water. After the lapse of some hours a slight excess of sulphuric acid is added, the mixture is allowed to settle for some time, filtered, and the acid is precipitated with barium chloride. It is filtered afresh, and evaporated on the water-bath until the hydrochloric acid of the barium salt is completely eliminated. The residue is taken up in absolute alcohol, and the solution is evaporated to dryness on the water-bath. The new residue, which is slightly acid, is dissolved in water, and exhausted with ether, which lays hold of fatty matters still contained in the liquid. The aqueous solution is rendered alkaline, again taken up with ether, and, after the evaporation of this solvent, the residue is treated with water acidulated with hydrochloric acid, which dissolves merely the alkaloids.

**Reagents for Sugar.**—M. Penzoldt.—Already noticed.

**Crystalline Aconitine.**—J. Williams.—From the *Chemist and Druggist.*

**A Reaction of Morphine.**—J. Donath.—From the *Journ. f. Prakt. Chem.*

**Sensitiveness of Smell.**—From the *Pharmaceutical Journal.*

No. 9, November 1, 1886.

**Researches on the Sugars.**—M. Berthelot.—Already noticed.

**The Nutritive Value of Edible Fungi.**—Th. Mœrner.—Of the total organic nitrogen present in Fungi a considerable proportion, in some cases 30 per cent, does not exist in a state capable of digestion.

**Variations of the Diastatic Action of the Saliva in Different Conditions.**—MM. Chittenden and E. Smith.

**On Cochineal and the Carmine of Commerce.**—C. Liebermann.—Already noticed.

**On Naringine.**—W. Will.—From the *Bull. de la Soc. Chimique.*

**The Fatty or Waxy Matter of Cinchona Barks.**—O. Hesse.—From *Liebig's Annalen.*

Wanted, for Germany, an experienced Foreman, practically acquainted with manufacture of Manures, Superphosphate, and Sulphuric Acid on a large scale. Must be accustomed to the supervision and control of workmen.—Apply, in German and English, with full particulars, to R. F., "Colombia," Mülheim am Rhein.

For Sale, quite new, LEAD PUMP, 4 inches diameter, 10 inches stroke, with dermatine bucket and valves, for pumping Sulphuric or other Acids; driving gear, pulleys, wall-brackets, &c., complete. Price low.—Spencer and Co., Lonsdale Chambers, Baldwin Street, Bristol.

The following Books Wanted.—Send Prices and Particulars to JAMES WALSER, Bookseller, 36, Western Road, Hove, Brighton.—"Jacob's Rod," a translation of a French work on the Divining Rod. Ashmole's "Theatrum Chemicum Britannicum." Ashmole's "The Way to Bliss." Raymond Lully's "Paracelsus," translated into English by R. Turner. "L'Abrege des Secrets Chymiques," by P. J. Fabre. Van Helmont's Works, folio, published 1664. "Lexicon Alchemiæ," by Rulando. "Hermetis, Egyptiorum et Chemicorum Sapientia." Helcher's "Dissertatio de Auro." "Hermippus Redivivus." "Lexicon Chymicum," by W. Johnson. "De Alchemia Dialogi Duo."

## PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

In the matter of an application by CHARLES DENTON ABEL, of 28, Southampton Buildings, Chancery Lane, W.C., for Letters Patent for "Improvements in the production of colouring matters or dyestuffs" (a communication), dated 1st January, 1886, No. 43.

NOTICE IS HEREBY GIVEN that the said Charles Denton Abel has applied for leave to amend the specification numbered as above.

A copy of the Specification as proposed to be amended can be inspected at the Patent Office, and full particulars of the proposed amendment were set forth in the Official Journal of the Patent Office issued on the 7th January, 1887.

Any person intending to oppose the said application must leave particulars of his objections thereto (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date hereof.

Dated this 8th day of January, 1887.

(Signed) H. READER LACK,
Comptroller-General.

ABEL IMRAY,
Agent for the Applicant,
28, Southampton Buildings, London, W.C.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

**Wet Extraction of Copper.**—Can any of your correspondents tell me the best published work in English treating or explaining the process of the wet extraction of copper from Spanish cupreous cinders?—J. N.

**Erythrosin.**—Can any of your readers inform me by whom and when "erythrosin" (tetra-iodo-fluorescein) was first discovered and described? Any references to original papers or other literature relating to this and other compounds of the eosin series will greatly oblige.—THETA.

## MEETINGS FOR THE WEEK.

MONDAY, 17th.—London Institution, 5.
—— Medical, 8.30.
TUESDAY, 18th.—Institution of Civil Engineers 8.
—— Pathological, 8.30.
WEDNESDAY, 19th.—Meteorological, 7. (Anniversary).
—— Society of Arts. 1. "Cameo-Cutting as an Occupation," by J. B. Marsh.
THURSDAY, 20th.—Royal, 4.30.
—— London Institution, 6.
—— Royal Society Club, 6.30.
—— Chemical, 8. "Some New Silicon Compounds and their Derivatives. I. The Action of Silicon Tetrabromide on Thio-Carbamide," by J. Emerson Reynolds, F.R.S. "Derivatives of Chromo-Organic Acids. I. On Certain Chromoxalates," by Emil A. Werner. "Remarks on Bayer's Paper 'On the Constitution of Benzene,'" by Dr. A. K. Miller.
FRIDAY, 21st.—Royal Institution, 8.
—— Society of Arts, 8. "The Upper Oxus," by Trelawney Saunders.
SATURDAY, 22nd.—Physical, 3.

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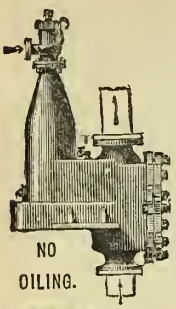

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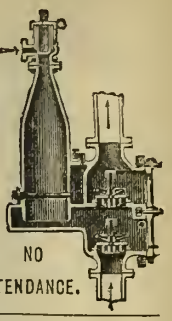

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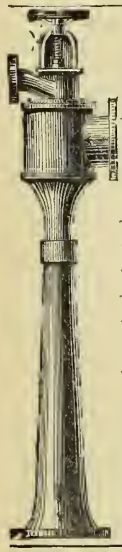

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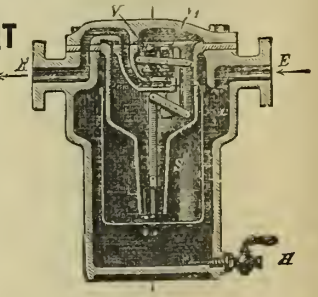


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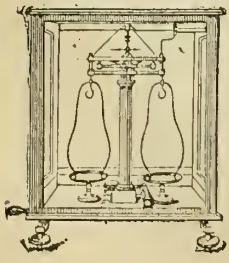

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THE CHEMICAL NEWS.

Vol. LV. No. 1417.

## ON THE CRIMSON LINE OF PHOSPHORESCENT ALUMINA.*

By WILLIAM CROOKES, F.R.S., V.P.C.S.

In a paper which I had the honour of communicating to the Royal Society† in March, 1879, I described the phosphorescence of alumina and its various forms when under the influence of the electrical discharge *in vacuo*, in the following words :—"Next to the diamond, alumina in the form of ruby is perhaps the most strikingly phosphorescent stone I have examined. It glows with a rich full red; and a remarkable feature is that it is of little consequence what degree of colour the earth or stone possesses naturally, the colour of the phosphorescence is nearly the same in all cases; chemically precipitated amorphous alumina, rubies of a pale reddish yellow, and gems of the prized 'pigeon's blood' colour, glowing alike in the vacuum, thus corroborating E. Becquerel's‡ results on the action of light on alumina and its compounds in the phosphoroscope. . . . The appearance of the alumina glow in the spectroscope is remarkable. There is a faint continuous spectrum ending in the red somewhere near the line B; then a black space, and next an intensely brilliant and sharp red line to which nearly the whole of the intensity of the coloured glow is due. . . . This line coincides with the one described by E. Becquerel as being the most brilliant of the lines in the spectrum of the light of alumina, in its various forms, when glowing in the phosphoroscope."

In 1881§ I again returned to the subject, describing a large number of fresh experiments; and I may add that the red glow of alumina has been, off and on, a subject of examination with me since the year first named down to the present time.

In the papers above quoted I gave as accurate measurements of the alumina line as my instrumental means would then permit. I have recently had occasion to go over these measurements again in a large spectroscope of very accurate construction, and the results, I think, are sufficiently important to be worth bringing before the notice of the Royal Society.

The spectrum consists firstly of an exceedingly faint and hazy pair of bands; these are too faint to measure, but they appear to be in about the same position as the bands 1986—2009, and 2031—2075 in the spinel spectrum given further on. Next is seen the characteristic crimson line of the alumina spectrum; this, when examined with a fine slit and high power eyepiece is seen to be double, the distance apart of the components being about half the distance separating the D lines. Then come a pair of fainter and rather nebulous orange lines; beyond them is a dark space followed by a continuous spectrum extending to the green. The following are the measurements of the spectrum :—

| Scale of Spectroscope. | $\lambda$. | $\frac{1}{\lambda^2}$ | Remarks. |
|---|---|---|---|
| 10·550° | 6942 | 2075 | The first component of the double crimson line. |
| 10·548° | 6937 | 2078 | The second component of the double crimson line. These lines are nearly as sharp as the components of D. |
| 10·450° | 6707 | 2223 | Approximate centre of a narrow band, shading off at each side. |
| 10·400° | 6598 | 2297 | Approximate centre of a narrow band, shading off at each side. This band is somewhat sharper and brighter than the one at 2223. |
| 10·360° | 6514 | 2357 | Approximate commencement of the continuous spectrum which extends into the green, shading off too indefinitely to admit of measurement. |

The accompanying cut (Fig. 1) gives the spectrum drawn to the $\frac{1}{\lambda^2}$ scale.

It is known that spinel (magnesium aluminate) phosphoresces with a red light, and shows a crimson line in its spectrum.* On examination in the high power spectroscope the spectrum of the light emitted by spinel under the radiant matter test is seen to differ from that emitted by ruby and alumina under the same test, and to closely approximate to the description given by E. Becquerel in 1859.

The spectrum first shows, in the extreme red, a faint double band, then a narrow crimson line, which, however, is not double, like the alumina line, neither is it quite so bright and sharp. Four hazy red bands follow, the fourth being wider and more indistinct than the others. Here the spectrum of most spinels fades away. Sometimes, however, a spinel is seen to glow with a greenish tint; in these the spectrum is the same as the others up to this point, and there is also seen a bright concentration of light in the green.

The measurements of the spinel spectrum are given in the following table :—

| Scale of Spectroscope. | $\lambda$. | $\frac{1}{\lambda^2}$ | Remarks. |
|---|---|---|---|
| 10·610° | 7096 | 1986 | Approximate commencement of first component of ill-defined double band. |
| 10·595° | 7055 | 2009 | Approximate end of ditto. |
| 10·580° | 7017 | 2031 | Commencement of ill-defined second component. |
| 10·550° | 6942 | 2075 | End of ditto. |
| 10·515° | 6857 | 2127 | Centre of sharp crimson line. |
| 10·490° | 6798 | 2164 | Approximate commencement of broad hazy band. |
| 10·450° | 6707 | 2223 | End of ditto. |
| 10·440° | 6683 | 2239 | Commencement of second component of group. |
| 10·405° | 6608 | 2290 | End of ditto. |
| 10·400° | 6598 | 2297 | Commencement of third component. |
| 10·380° | 6555 | 2327 | End of ditto. This band is somewhat sharper and brighter than the other components of this group. |
| 10·370° | 6534 | 2342 | Commencement of fourth component of ditto. |
| 10·330° | 6454 | 2401 | End of ditto. |
| 9·730° | 5541 | 3257 | Approximate commencement of luminous concentration in the green seen in some spinels. |
| 9·440° | 5234 | 3650 | Position of maximum luminosity of this concentration of light. From this point the spectrum appears to be continuous, shading off gradually towards the blue and violet. |

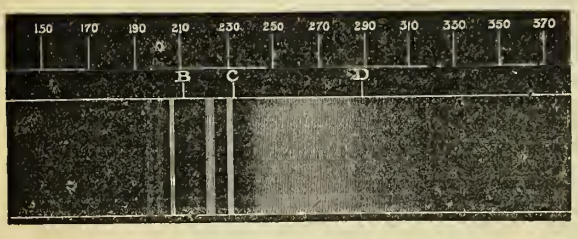
* A Paper read before the Royal Society, January 13th, 1887.
† *Phil. Trans.*, Part 2, 1879, pp. 660, 661.
‡ *Annales de Chimie et de Physique*, vol. lvii., 1859, p. 50.
§ *Proc. Roy. Soc.*, vol. xxxii., pp. 206—208.

* E. Becquerel, *Annales de Chimie et de Physique*, vol. lvii., p. 58. W. Crookes, *Proc. Roy. Soc.*, vol. xxxii., p. 208.

The drawing (Fig. 2) shows the spectrum, drawn to the $\frac{1}{\lambda^2}$ scale.

In the *Comptes Rendus* for December 6th last* appears a brief note by M. de Boisbaudran, in which he announces, "*to take date, that alumina, calcined and submitted to the electrical discharge in a vacuum, has not given him a trace of red fluorescence. This fluorescence, as well as its special spectrum, shows itself brilliantly when the alumina contains* 1-100*th and even* 1-1100*th of* $Cr_2O_3$. *With the* 1-10,000*th part of* $Cr_2O_3$ *we still obtain very visible rose colour. . . . From these observations the presence of chromium appears to be indispensable to the production of the red fluorescence of alumina.*"

Fig. 1.




The Alumina Spectrum.

This statement being opposed to all my experience, I immediately instituted experiments with a view, if possible, to clear up the mystery. I started with aluminium sulphate, which I knew to be tolerably pure, and in which ordinary tests failed to detect chromium. On ignition and testing in the usual manner in a radiant matter tube, the alumina line was brightly visible in the spectrum of the emitted light. Different portions of this aluminium sulphate were now purified by various processes for the separation of chromium. All gave as a result the absence of this impurity. The most trustworthy process being that devised by Wöhler,† I used it to purify the bulk. The salt was dissolved in water, and excess of caustic potash added till the precipitate first formed re-dissolved. Chlorine was now passed through till no more precipitate fell down and the liquid retained a strong odour of chlorine. The whole of the chromium would now be in solution, whilst the alumina would be in the precipitate. The alumina was filtered off, well washed, and a portion tested in the radiant matter tube. It gave as good an alumina spectrum as did the original sulphate; the crimson line being very prominent.

The alumina thus purified was a second time dissolved in caustic potash and submitted to the chlorine purification. Again in the radiant matter tube the alumina gave its characteristic crimson line spectrum.

The filtrate from the alumina, which should contain all the chromium present in the form of potassium chromate, was supersaturated with hydrochloric acid and boiled till free from volatile chlorine compounds. Alcohol was then added, and it was again boiled to reduce to the state of sesquichloride of chromium any chromic acid which might be present. Ammonia in excess was now added, and the whole was boiled; a very small precipitate of a brownish colour fell down; it was filtered and washed. This precipitate, which was not more than the 1·50,000th part of the alumina from which it was derived, contained no chromium whatever; it was too small in quantity to admit of a complete analysis being made, but all the tests which I could apply showed it to be a mixture of ferric oxide and alumina.

One part of this precipitate was mixed with 100 parts of the pure alumina from which it had just been separated, and the mixture was tested in the radiant matter tube. The phosphorescence was the same as in the two previous experiments, the crimson line being neither better nor worse.

I now prepared aluminium chromate and tested its action in the radiant matter tube. It was almost black after ignition and refused to phosphoresce. A mixture was then made of aluminium chromate and alumina in the proportion of one part chromium to 100 parts of aluminium. After ignition the colour of the mixture was almost white. Tested, it gave very poor phosphorescence; the alumina line was faintly visible.

Aluminium acetate was mixed with 5 per cent of ammonium bichromate, ignited with sulphuric acid, and tested in the radiant matter tube. There was no phosphorescence. The same mixture was heated to a high temperature before the blowpipe, when it gave a very feeble phosphorescence, but I could detect no line in the spectrum.

Fig. 2.

Spectrum of Spinel (Magnesium Aluminate).

Pure alumina was mixed with 5 per cent of ammonium bichromate and moistened with sulphuric acid. After ignition it phosphoresced with a reddish colour and the spectrum showed a concentration of light in the orange, but no alumina light was visible. The tube was opened and the contents heated to a very high blowpipe temperature. In the radiant matter tube it gave the same results as before.

A mixture of 0·5 per cent ammonium bichromate, 10 per cent of lime, and 89·5 per cent of pure alumina was ignited with sulphuric acid and tested in the usual way. The calcium brought out a trace of yttrium and samarium bands, but no crimson line was to be seen.

Alumina precipitated from its ammoniacal solution by boiling was found to glow with a green light in the vacuum tube and to give no crimson line in its spectrum. The tube was now opened and some of its contents removed and heated in a hot blast blowpipe to the melting-point of platinum for about five minutes. Re-tested in a vacuum tube this alumina was seen to glow at the points and edges of the lumps, where the heat had been fiercest, with a red light, giving a faint line spectrum. The bulk of the mass, however, gave out the original green glow.

To get the crimson line most brilliantly it is necessary to ignite the earth to the highest temperature of the blowpipe

* *Comptes Rendus*, vol. cii., p. 1107.

† "Select Methods in Chemical Analysis," 2nd edition, p. 124.

flame. With a slightly less heat the phosphorescence is not strong and the line is faint. When the temperature has not been raised high enough the colour of the emitted light in most aluminas is green, and no line is visible; whilst the same earth raised to a higher temperature glows with a red light, and the red line comes into view. The most brilliant crimson line, when seen at all, has always been obtained when the alumina has been kept near the melting-point of platinum for some time. Physical differences, or perhaps even difference in molecular composition, also exert a great influence on the phosphorescence of alumina. In this connection I ask permission to quote a sentence from my paper of May, 1881, already mentioned:—"Two earthen crucibles were tightly packed, the one with sulphate of alumina, the other with acetate of alumina. They were then exposed, side by side, to the most intense heat of a wind-furnace—a heat little short of the melting-point of platinum. The resulting aluminas were then tested in the molecular stream. The alumina from the sulphate gave the crimson glow and the spectrum line. The alumina from the acetate gave no red glow or line, but a pale green phosphorescence."

Experience gained in the yttria research has taught me that the possibility of the molecule of aluminium being composed of two or more sub molecules, only one of which is capable of giving the crimson line phosphorescence, must not be overlooked. To test this hypothesis alumina, as pure as I could prepare it, was submitted to three separate processes of fractionation, the operations in each case being repeated from 20 to 30 times. Alumina giving the crimson line always concentrated towards one end of the fractionations, whilst at the other end the alumina sometimes phosphoresced of a green tint, and at others scarcely phosphoresced at all, the crimson line being either very feeble or entirely absent in the spectrum. The earths were always ignited for the same time and, as nearly as possible, to the same temperature.

In no case could chromium be detected at either extremity of the fractionations.

These experiments are perhaps too few to permit any important inference being drawn from them. There seem, however, to be four possible explanations of the phenomena observed:—

1. The crimson line is due to alumina, but it is capable of being suppressed by an accompanying earth which concentrates towards one end of the fractionations.
2. The crimson line is not due to alumina, but is due to the presence of an accompanying earth concentrating towards the other end of the fractionations.
3. The crimson line belongs to alumina, but its full development requires certain precautions to be observed in the time and intensity of ignition, degree of exhaustion, or its absolute freedom from alkaline and other bodies carried down by precipitated alumina, and difficult to remove by washing; experience not having yet shown which of these precautions are essential to the full development of the crimson line and which are unessential.
4. The earth alumina is a compound molecule, one of its constituent molecules giving the crimson line. According to this hypothesis alumina would be analogous to yttria.

It is not unlikely that a chemist wishing to obtain alumina of exceptional purity might submit it to a series of operations, akin to fractionation, which would have the effect of giving earths phosphorescing either with a strong crimson line, or with little or no crimson line; and either of these samples of alumina might be looked upon by him as pure. It is possible that some such explanation as this may be at the bottom of the contradictory statements respecting the crimson line of alumina.

## SOME RECENT RESEARCHES ON THE NATURE OF THE NITROGENOUS ORGANIC MATTER OF SOILS.

By R. WARINGTON.

In the present communication I propose to describe, in the first place, the general results of some very incomplete experiments of my own, made in the Rothamsted Laboratory, and hitherto unpublished; and, in the next place, to call attention to some recently published investigations of considerable importance, bearing on the same subject.

In February, 1883, I made a few experiments to ascertain, if possible, whether amides were present in soil. The soil selected was one rich in nitrogenous matter, having been manured annually with farmyard manure for thirty-eight years. In contained when dry 0·189 per cent of nitrogen. 300 grms. of the dry, finely-powdered soil, were extracted with ammonia-free water on a vacuum filter, after the manner described in *Trans. Chem. Soc.*, 1882, 354. The first extract of 100 c.c. was evaporated to dryness, after being made faintly alkaline with lime-water. The residue left by the watery extract was transferred with a little hot water into Frankland's nitrometer, previously filled with mercury; 5 c.c. of freshly-prepared solution of sodium hypobromite were then introduced. A little gas was evolved in the cold, and more on boiling the aqueous solution with a spirit-lamp. The gas evolved was found to contain 0·000464 grm. of nitrogen. A second watery extract of the same soil gave only a trace of nitrogen when treated in the same manner.*

The residues of a first and second watery extract from the same soil, prepared as above described, but on another occasion, were treated with acetic acid in a flask connected with a Sprengel pump; tubes containing beads moistened with a strong solution of sodium hydrate intervening between the flask and the pump. On the completion of a vacuum, a solution of potassium nitrite, previously contained in a side tube of the flask, was allowed to run in; the gas evolved was collected and analysed. The gas from the first watery extract of 300 grms. of soil contained 0·000719 grm. of nitrogen; the gas from the second extract 0·000343 grm.

There was thus evidence, both from the reaction with hypobromite, and with nitrous acid, of the presence of a very small quantity of soluble amide in the soil.

The soil which had been extracted with water was next treated with 12 grms. of potassium carbonate, and water again passed through the soil, which remained on the vacuum filter. The highly coloured alkaline extract was re-passed through the soil till the action was apparently completed. The alkaline extract was then shaken with a considerable volume of ether, the ethereal solution being finally separated, and the ether removed by distillation. After treatment with ether, the potassium carbonate solution was acidified with sulphuric acid, and again shaken with ether, the matter dissolved by ether being separated as before. Both quantities of 300 grms. of soil were treated in this way.† The residues of the ether extracts were in one case heated with sodium hypobromite, and in the other case were treated with acetic acid and potassium nitrite, as above described. In no case was any appreciable quantity of nitrogen gas obtained.

It would appear from these results that the potassium

* Sodium hypobromite readily attacks many amides. Asparagine, at a boiling-heat, appears to give up half its nitrogen. If the asparagine has been converted into aspartic acid by heating with hydrochloric acid, and the ammonia formed has been removed by evaporation with an alkali, no nitrogen is produced on heating with hypobromite. When heating a sodium hypobromite solution over mercury, oxygen gas is often evolved, and must be separated before measuring the nitrogen.

† The extraction of the alkaline and acid solutions with ether, as a means of separating basic and acid amides, was suggested to me by Mr. D. A. Louis.

carbonate extract from the soil did not contain amido bases or acids soluble in ether.

The acid solution obtained by adding sulphuric acid to the potassium carbonate extract was submitted to some qualitative tests. Phospho-tungstic acid gave a large precipitate in the solution. This precipitate was proved to contain nitrogen, but no quantitative analysis was made.

G. Loges (*Landw. Versuchs. Stationen*, 1886, xxxii., 201) has stated that the hydrochloric acid extract of soils yields a precipitate with phospho-tungstic acid. He found the ratio of nitrogen to carbon in this precipitate to be about 1 : 6·2 c.c. Further investigation of the subject is promised. Phospho-tungstic acid is a well-known reagent for the precipitation of peptones; its behaviour towards other soluble nitrogenous bodies seems to have been but little studied.

I must next briefly refer to some experiments of my own on the extraction of the nitrogenous matter of soil with hydrochloric acid; these experiments were made between October, 1885, and March, 1886. The soil, and subsoil, of an ordinary arable field was dried and powdered. 400 grms. were shaken during several days with 1000 c.c. of dilute hydrochloric acid. The solution was filtered; ammonia was determined in a part of the solution by distillation with magnesia, and total nitrogen was determined in another portion of the solution by Kjeldahl's method. The hydrochloric extract was for this purpose evaporated to dryness, with a few drops of ferrous chloride (to destroy nitrates), in a glass basin; the residue was heated in a chloride of calcium bath in order to more completely dry it; 10 c.c. of oil of vitriol were then added; the glass basin was then covered with a clock-glass, and heated on a sand-bath to near the boiling-point of the sulphuric acid. When the mass was almost colourless, powdered potassium permanganate was sprinkled in and heating continued for a short time. The whole mass was finally transferred to a large flask, provided with a funnel-tube and exit-tube, the latter connected with the tin worm of a condensing apparatus. Strong soda solution, previously boiled, was introduced through the funnel-tube, the contents of the flask boiled, and the ammonia evolved collected in dilute sulphuric acid. This method was found far more accurate than combustion with soda lime for the purpose of determining small quantities of nitrogen.

The special object of these experiments does not concern us in the present paper. The general result was that the hydrochloric acid removed from the soil considerable amounts of nitrogenous organic matter, the amount increasing with the length of contact, and with the strength of the acid. Both soils and subsoils were in some cases treated four successive times with hydrochloric acid, but in no case was there any appearance of an exhaustion of the nitrogenous matter rendered soluble. All the experiments were made in the cold. The greatest strength of hydrochloric acid employed was 5 per cent by volume of the concentrated liquid acid. No ammonia determinations were made save in the first extract. It will be seen immediately that other investigators have obtained very important results by a more complete study of the action of hydrochloric acid.

Baumann states (*Forschungen auf den Gebiete der Agrikultur-Physik*, 1886, 283) that when soils are boiled for two hours with very dilute hydrochloric acid ammonia is produced, the quantity exceeding by ten or twelve times that pre-existing in the soil.

Berthelot and André (*Compt. Rend.*, Dec. 6, 1886, 1101) have studied the action of hydrochloric acid on soil far more thoroughly. They find that it splits up the insoluble nitrogenous matter, producing ammonia, and soluble nitrogenous matter. The action is greater the greater the strength of the acid, the longer its contact with the soil, and the higher the temperature. The action of a solution containing 20 per cent by volume of the ordinary liquid hydrochloric acid is very considerable. A soil containing 0·174 per cent of nitrogen, boiled for two hours with this acid, gave up 31·8 per cent of its nitrogen; of this amount 7·1 was ammonia, produced by the action of the acid. The proportion of the nitrogen liberated as ammonia, to that remaining in organic combination dissolved by the acid, was about 1 : 3.

From these results, coupled with the well-known production of ammonia when soil is attacked by alkalies, even in the cold, Berthelot and André conclude that the nitrogenous matter of soil consists chiefly of insoluble amides; these by the action of acids, alkalies, or even water, are split up into ammonia and soluble amides. The amides dissolved in the hydrochloric acid they consider to form two classes: (1) those precipitated along with ferric oxide and calcium salts when the acid is neutralised by potash, and (2) those remaining dissolved in the neutralised liquid.

The behaviour of the nitrogenous matter of soil to acids and alkalies is certainly so similar to that exhibited by amides generally, as to render the views of Berthelot and André highly probable. Nor is evidence wanting of the synthesis of amides of the class supposed to exist. The disappearance of ammonia during the fermentation of fresh farmyard manure has been often noticed. Joulie (*Annales Agronomique*, 1884, 297) found that in a mixture of known composition, consisting of finely-divided straw, horse dung, and ammoniacal urine, the large amount of ammonia present at starting steadily diminished, while there was a gradual increase in the organic nitrogen, which was finally 35 to 63 per cent in excess of the amount originally present. We have here, probably, a synthesis of insoluble amides from ammonia and humic acids.

It is, of course, by no means proved as yet that the whole of the organic nitrogen in soils is of an amide nature; for this and other branches of the subject we must await the result of further investigation. The work already done certainly throws much new light on a hitherto obscure subject, and the chief credit of this must be awarded to MM. Berthelot and André.

## THE ABSORPTION OF NITRIC OXIDE BY SULPHURIC ACID.

By F. NETTLEFOLD, F.C.S.

The recent controversy on this subject leaves practical workers much in doubt regarding the correction to apply for this source of error; for it is difficult to understand that no solution of $N_2O_2$ in $H_2SO_4$ can take place.

The following results seem to point to the cause of many of the apparent anomalies.

*Solutions of Different Samples of Gun-Cotton in* $H_2SO_4$.

0·3 grm. in 7 c.c. $H_2SO_4$ gave 59·7 c.c. of $N_2O_2$.
16·7 c.c. added „ 58·4

The 16·7 c.c. „ absorbed 1·3 per c.c. of $H_2SO_4$, 0·08 c.c. of $N_2O_2$.

0·3 grm. in 8·3 c.c. $H_2SO_4$ gave 58·84 c.c. of $N_2O_2$.
15·7 c.c. added „ 54·94

The 15·7 c.c. „ absorbed 0·90 per c.c. of $H_2SO_4$, 0·057 c.c. of $Na_2O$.

0·42 grm. in 16·7 c.c. $H_2SO_4$ gave 58·4 c.c. of $N_2O_2$.
10·6 c.c. added „ 57·8

The 10·6 c.c. „ absorbed 0·60 per c.c. of $H_2SO_4$, 0·057 c.c. of $N_2O_2$.

*Potassic Nitrate Dissolved in Sulphuric Acid.*

0·25 grm. air dry in 8·7 c.c. $H_2SO_4$ gave 53·7 c.c. of $N_2O_2$.
12 c.c. added „ 51·3

The 12 c.c. „ absorbed 2·4 per c.c. of $H_2SO_4$, 0·2 of $N_2O_2$.

0·25 grm. dry in 7·9 c.c. $H_2SO_4$ gave 58·91 c.c. of $N_2O_2$.
15·1 c.c. added ,, 57·51

The 15·1 c.c. ,, absorbed 1·4 per c.c. of $H_2SO_4$, 0·093 $N_2O_2$.

It will be seen that there is considerable variation in the absorption of nitric oxide by the sulphuric acid, being much less in the case of gun-cotton than in that of potassic nitrate.

Working under precisely similar conditions, results can be obtained corresponding in the first place of decimals, being a most reliable and constant method for nitrogen determinations. But in working in researches where the exact amounts of nitrogen are required, some correction should be made. And it appears that a special correction is required for each substance experimented on.

A sample of pure $N_2O_2$ was collected over mercury direct into the nitrometer, and $H_2SO_4$ was added through the funnel stopcock.

With 8·2 c.c. of $H_2SO_4$, volume of gas .. 41·85
After shaking and standing one hour .. 41·80

So that no absorption seems to take place with the pure gas, though, before shaking, a slight contraction takes place.

The sulphuric acid was sp. gr. 1·842.

The gases measured, at 0° C., 8760 m.m. of mercury.

## A METHOD FOR THE SEPARATION OF SODIUM AND POTASSIUM FROM LITHIUM BY THE ACTION OF AMYL ALCOHOL ON THE CHLORIDES,

### With some Reference to a Similar Separation of the Same from Magnesium and Calcium.*

By F. A. GOOCH.

(Continued from page 19.)

When aqueous solutions of sodium chloride or potassium chloride are treated with amyl alcohol and boiled, the water disappears, as before, leaving first a globule of the concentrated solution, and finally the crystalline salts. On continuing the boiling until a thermometer, dipped in the liquid, indicates the temperature at which the alcohol boils by itself, a slight additional precipitation, doubtless due to the expulsion of the water retained by the alcohol up to this point, takes place upon the walls of the containing vessel. The results of quantitative tests of the solubility of sodium and potassium chlorides are given in the following tables. The strength of the solutions of sodium chloride and potassium chloride were determined by evaporating weighed portions in a platinum crucible and drying at a temperature considerably below the melting-point of the salt, and weighing. The solution of lithium chloride was standardised by treating a weighed portion with sulphuric acid in excess, evaporating, igniting at red heat, and weighing. The standards were fixed by experiments (1) to (9).

| | Weight of Solution of NaCl taken. Grm. | Weight of NaCl found. Grm. | Weight of NaCl in 10 grms. of solution. Grm. | Mean. Grm. |
|---|---|---|---|---|
| (1) | 10·7110 | 0·1072 | 0·1001 | |
| (2) | 10·9419 | 0·1097 | 0·1003 | 0·1002 |
| (3) | 10·9325 | 0·1097 | 0·1003 | |

| | Weight of Solution of KCl taken. Grm. | Weight of KCl found. Grm. | Weight of KCl in 10 grms. of solution. Grm. | Mean. Grm. |
|---|---|---|---|---|
| (4) | 9·3045 | 0·1744 | 0·1874 | |
| (5) | 10·7225 | 0·2006 | 0·1871 | 0·1872 |
| (6) | 11·1974 | 0·2096 | 0·1872 | |

* *Proceedings of the American Academy of Arts and Sciences*, 1886-1887.

| | Weight of Solution of LiCl taken. Grm. | Weight of $Li_2SO_4$ found. Grm. | Weight of LiCl in 10 grms. of Solution. Grm. | Mean. Grm. |
|---|---|---|---|---|
| (7) | 10·9280 | 0·1635 | 0·1156 | |
| (8) | 11·1480 | 0·1665 | 0·1153 | 0·1154 |
| (9) | 10·8790 | 0·1626 | 0·1154 | |

To determine the solubility of sodium chloride and potassium chloride in amyl alcohol, portions of the test solutions were weighed out, evaporated to a convenient bulk in platinum crucibles of 100 c.m.³ capacity, amyl alcohol was added, the water expelled by boiling, and the heating continued for some minutes after the thermometer in the liquid indicated 132° C., the boiling point of the alcohol employed. The liquid was then decanted with care and the residue dried at a temperature below its melting-point, and weighed. When the chlorides are precipitated in the manner described, the deposit generally adheres so closely, and such particles as do remain loose settle so well, that the supernatant liquid may be decanted to the end without appreciable transportation of the insoluble residue. For the sake of perfect security, however, in this part of the manipulation, the decanted liquid was filtered under gentle pressure upon asbestos, with the aid of the device which I have previously described for such purposes,* and, after gentle heating, the increase in weight of the felt and the containing perforated crucible added to the weight of the residual salt. In no case did this increase exceed a few tenths of a milligrm., and often could not be detected.

As a source of heat, a bath in which the sand of the sand-bath is replaced by smooth asbestos board is a convenience, or a piece of asbestos board simply, about 30 c.m. square, supported by a broad tripod and heated under the middle by a Bunsen burner, answers equally well to secure every gradation of heat without danger of igniting the evaporated alcohol.

As a control upon the results obtained by weighing the residue as described, the filtrate was evaporated in a large platinum crucible, and the residue thus left gently heated and weighed. Though the evaporation be conducted with extreme care, the residue is almost sure to show some blackening, due to the carbonisation of matter carried by the alcohol, which will not disappear entirely without the application of a degree of heat which the salts cannot bear without danger of volatilisation. The weight of the residue from the amyl alcohol itself is small,—one portion of 50 c.m.³ yielding 0·0003 grm., and its mate 0 0007 grm. —so that the data obtained by the evaporation of the filtered alcohol of the experiments, if not quite so trustworthy as the former testimony, may nevertheless serve the purpose of a very close control. Both sets of data are given in the following table.

| | Weight of NaCl taken. Grm. | Total Weight of NaCl found. Grm. | Weight found in Residue. Grm. | Weight found in Solution. Grm. | Vol. of residual Amyl Alcohol. C.m.³ |
|---|---|---|---|---|---|
| (10) | 0·1062 | 0·1067 | 0·1043 | 0·0024 | 52 |
| (11) | 0·1043 | 0·1047 | 0·1024 | 0·0023 | 46 |
| (12) | 0·1024 | 0·1030 | 0·1003 | 0·0027 | 51 |
| (13) | 0·1003 | 0·1008 | 0·0983 | 0·0025 | 45 |

Reducing these figures to a common level to show the action of the same amount of amyl alcohol, in every case we have :—

| | Loss of NaCl to 100 c.m.³ of Amyl Alcohol. Grm. | Mean. Grm. | Weight of NaCl found in Solution in 100 c.m.³ of Amyl Alcohol. Grm. | Mean. Grm. |
|---|---|---|---|---|
| (10) | 0·0037 | | 0·0046 | |
| (11) | 0·0041 | 0·0041 | 0·0050 | 0·0051 |
| (12) | 0·0041 | | 0·0053 | |
| (13) | 0·0044 | | 0·0055 | |

* *Proceedings of the American Academy of Arts and Sciences*, vol. xiii., p. 342.

| | Weight of KCl taken. Grm. | Total Weight of KCl found. Grm. | Weight found in Residue. Grm. | Weight found in Solution. Grm. | Vol. of residual Amyl Alcohol. C.m.³ |
|---|---|---|---|---|---|
| (14) | 0·2091 | 0·2093 | 0·2074 | 0·0019 | 35 |
| (15) | 0·2074 | 0·2078 | 0·2059 | 0·0019 | 36 |
| (16) | 0·2059 | 0·2059 | 0·2040 | 0·0019 | 32 |
| (17) | 0·2040 | 0·2041 | 0·2015 | 0·0026 | 45 |

Derived from these figures we have :—

| | Loss of KCl to 100 c.m.³ of Amyl Alcohol. Grm. | Mean. Grm. | | Weight of KCl found in Solution in 100 c.m.³ of Amyl Alcohol. Grm. | Mean. Grm. |
|---|---|---|---|---|---|
| (14) | 0·0049 | 0·0051 | | 0·0054 | 0·0056 |
| (15) | 0·0041 | | | 0·0053 | |
| (16) | 0·0059 | | | 0·0059 | |
| (17) | 0·0056 | | | 0·0058 | |

From these figures it appears that the total weight of chloride found is always a little greater than that taken, the mean increase being 0·0005 grm. for sodium chloride and 0·0002 grm. for potassium chloride. It appears also that the residue left by the evaporation of the decanted and filtered amyl alcohol is greater than the loss put upon the chloride by the treatment—in the case of sodium chloride 0·0005 grm., in the mean, for every 50 c.m.³ of amyl alcohol, which is about the quantity employed in the experiments; for potassic chloride 0·0002 grm., in the mean, for 40 c.m.³ of amyl alcohol, which is approximately the quantity used in that case. It will be seen, therefore, that there exists for both salts an exact coincidence between the mean total excess found and the difference between the figures which indicate the solubility of the salts for the two methods of determination; and, taking this fact in conjunction with the results of the evaporation of amyl alcohol in blank—the mean residue being 0·0004 grm. for 40 c.m.³ and 0·0005 grm. for 50 c.m.³—it seems to be brought out pretty clearly that the former set of figures represents more exactly the solubility of the salts, though the difference between the two series is not great. Resting, then, upon the former determinations, the solubility of sodium chloride may be taken as 0·0041 grm. in every 100 c.m.³ of anhydrous amyl alcohol, or one part in 30,000 parts by weight; and the solubility of potassium chloride, a little greater, is 0·0051 grm. to 100 c.m.³ of amyl alcohol, or one part in 24,000 by weight.

The conditions under which the salts are acted upon are such as should insure the complete saturation of the solvent, and in this connection it is interesting to note that, for the quantities of material employed, the discrepancy between comparable figures never exceeds 0·0005 grm.

In experiments (10), (11), and (14), (15), the alcohol was decanted and filtered at once while hot; in (12), (13), and (16), (17), it was cooled to 30° C. before decanting; so it appears that the solubility of the salts is not influenced by changes of temperature within the range from 'C. to 132° C.

To be continued).

## ANALYSES OF COMMERCIAL FERTILISERS.*

(Continued from p. 21.)

Dr. Gascoyne presented the following Table, giving the results obtained on a variety of fertilising material by the soda-lime method; the method suggested by Professor Johnson, using slaked lime as a substitute for soda-lime; the Ruffle method, and a modification of the Ruffle method, using slaked lime instead of soda-lime, described in full in the report of the nitrogen committee on methods to be used for the determination of nitrogen during the next year. (See Table, next page).

Dr. Gascoyne stated that he had made a number of tests by the modified Ruffle method, using potassium xanthogenate as a substitute for the charcoal and sulphur mixture with good results.

Discussion of the report and papers being in order,

Dr. Jenkins gave it as his experience that the Kjeldahl method gave identical results with the absolute method in the absence of nitrates. Coarse bone, high grade blood, and wheat bran gave results from one to three-tenths per cent higher than with soda-lime. He had also obtained good results with ferro- and ferri-cyanide of potassium, and found that on pure ammonia salts the absolute and Kjeldahl methods agreed. A source of error to be avoided in the latter method was the presence of ammonic sulphate in the sulphuric acid used.

Dr. Chazal considered the committee's samples as an unfair test of the Ruffle method, as they contained nitrate in only one instance.

Professor Lupton said—We have found in my laboratory the Kjeldahl method unreliable in the case of nitrates, but satisfactory in other cases. One great objection to the method is the length of time required for digestion with sulphuric acid. From twelve to fifteen hours were necessary in the case of the samples sent out by the committee.

Dr. Gascoyne then spoke in favour of the use of dry slaked lime and crystallised hyposulphite instead of the committee's mixture; and

Dr. White expressed his approval of the former, using enough sodic hydrate, however, to make the lime more compact and granular.

It was then resolved that, in the absence of Dr. Dabney, the Chair should appoint some one to fill his place to act with the remainder of the committee in preparing recommendations for the ensuing year.

Dr. Gascoyne was appointed.

While awaiting the recommendations of the several committees as to methods to be adopted by the Association, by unanimous consent Mr. de Gnequier was allowed to address the convention.

Mr. de Ghequier said :—

Gentlemen—I have the honour to respectfully submit on behalf of the National Fertiliser Association the request of the committee on legislation, to the effect that you may be pleased to pass before adjourning, a resolution by which, as an association of official chemists, you will indorse the incorporation of such amendment to Senate Bill 372 (H. R. 2933) as will secure the adoption of that method of analysis which you from time to time may decide upon, in all States desiring to obtain the appropriation of 5000 dols. per annum for either agricultural experiment stations or agricultural colleges, and secure likewise one uniform mode of regulation brand, and, above all, uniformity in branding bags, together with an abolition of commercial valuations. Our Association, from its close intercourse with the members of your Association, thoroughly appreciates the sentiments which from time to time have been expressed by you on this very subject, and because it is aware of the fact that your views coincide fully on this matter with those entertained by the trade, the committee on legislation indulges in the hope that the request now preferred to put your opinions in a tangible form on record so as to enable us to urge on solid grounds the passage of such amendments as will procure for the trade the possibility to have for one brand only one bag will meet with a favourable reception. The multiplication of State laws increases yearly the number of bags a manufacturer has to keep on hand, and exposes him uselessly to lawsuits and losses without any benefit whatsoever accruing from this variety of expressions to the farmer. On the contrary, the views of the vast majority of the members of your Association clearly indicate that you not only recognise the justice of our desire to see an absurdity replaced by a provision more in accord with the dictates of common sense, but are disposed to assist us in this direction. The opportunity to do so in an efficient

* From the *Proceedings* of the Third Annual Convention of the Association of Official Agricultural Chemists, at Washington, D.C., August 26 and 27, 1886. Edited by Clifford Richardson, Secretary.

| | Soda-lime. | | Slaked lime. | | Ruffle method. | | Ruffle method modified. | |
|---|---|---|---|---|---|---|---|---|
| | Per ct. | Average. | Per ct. | Average. | Per ct. | Average. | Per ct. | Avge. |
| Ammoniated superphosphate .. | 1·67 | | 1·64 | | 1·63 | | 1·66 | |
| | 1·69— 1·68 | | 1·68— 1·66 | | 1·69— 1·66 | | 1·70— 1·68 | |
| ,, ,, .. .. | 1·94 | | 1·97 | | 1·97 | | 1·97 | |
| | 1·98— 1·96 | | 1·99— 1·98 | | 2·03— 2·00 | | 2·01— 1·99 | |
| Bone meal.. .. .. .. .. .. | 4·10 | | 4·07 | | 4·13 | | 4·15 | |
| | 4·14— 4·12 | | 4·11— 4·09 | | 4·17— 4·15 | | 4·15— 4·15 | |
| Cotton-seed meal .. .. .. .. | 7·35 | | 7·30 | | 7·40 | | 7·38 | |
| | 7·39— 7·37 | | 7·36— 7·33 | | 7·46— 7·43 | | 7·42— 7·40 | |
| Dried blood .. .. .. .. .. | 12·23 | | 12·27 | | 12·31 | | 12·33 | |
| | 12·31—12·27 | | 12·31—12·29 | | 12·39—12·35 | | 12·41—12·37 | |
| Azotin .. .. .. .. .. .. | 12·98 | | 12·98 | | 13·03 | | 13·05 | |
| | 13·04—13·01 | | 13·02—13·00 | | 13·09—13·06 | | 13·11—13·08 | |
| Fish scrap.. .. .. .. .. .. | 8·12 | | 8·13 | | 8·14 | | 8·12 | |
| | 8·18— 8·15 | | 8·17— 8·15 | | 8·22— 8·18 | | 8·18— 8·15 | |
| Castor pomace.. .. .. .. .. | 4·98 | | 4·98 | | 5·00 | | 5·00 | |
| | 5·04— 5·02 | | 5·02— 5·00 | | 5·04— 5·02 | | 5·06— 5·03 | |
| Peruvian guano .. .. .. .. | 7·46 | | 7·45 | | 7·51 | | 7·50 | |
| | 7·50— 7·48 | | 7·49— 7·47 | | 7·55— 7·53 | | 7·56— 7·53 | |
| Ammoniated superphosphate with 1 p.c. of nitrogen from nitrate .. | | | | | 4·30 | | 4·32 | |
| | | | | | 4·36— 4·33 | | 4·40— 4·36 | |
| Ditto ditto .. | | | | | 6·44 | | 6·44 | |
| | | | | | 6·52— 6·48 | | 6·48— 6·46 | |
| Ground tobacco stems .. .. .. | | | | | 1·54 | | 1·50 | |
| | | | | | 1·58— 1·56 | | 1·54— 1·52 | |
| Commercial nitrate of soda.. .. | | | | | 15·90 | | 15·91 | |
| | | | | | 15·96—15·93 | | 15·99—15·95 | |

way now presents itself, and hence the request of our Association for the passage of a resolution indorsing Senator Chace's amendment.

Nearly 10,000,000 bags are consumed by the trade, and some firms use upwards of 300,000. For four brands four bags would suffice; at present, however, it is necessary to keep a stock at least sixty to a hundred on hand. It is a hardship the greatness of which no one can properly realise except those who during the rush of a shipping season witness the trouble and annoyance which is daily incurred on that ground.

The very science—agricultural chemistry—which has called the fertiliser industry into being should certainly not be the means of throwing superfluous obstacles in the way of the prosecution of that business, and the time has arrived, it seems to me, when to the signal services rendered by agricultural chemistry to the trade in a scientific way proper assistance in a business way should be granted by removing what you yourselves admit to be entirely useless obstructions. As regards commercial valuations, it will ever remain an impossible attempt to impress upon the farmer that they represent only a means of comparing prices, but do not represent either the agricultural value of fertilisers or the figure at which a manufacturer should sell his goods. It is carrying the paternal government theory too far, and experience has shown that no good has thereby been accomplished. If the farmer is incompetent to judge from the analysis what is and what is not a good article, why is his ignorance not in a similar way assisted in the many other articles which he is bound to purchase. Flour, agricultural implements, boots and shoes, prints, &c., might, with precisely the same justice, and on precisely the same ground, have commercial valuations attached, and I think it would be quite a surprise to farmer and scientist to see what an enormous margin of profit there is in nearly every commodity and how comparatively insignificant the same margin is on fertilisers. Commercial valuations can hardly be said to be more than a discrimination against the very industry which has done more to build up a greater productiveness of the soil than all others put together. On this point, however, there has so much been said that it is quite familiar to you that I forego to dwell upon this subject.

Our Association is in hearty accord with the bill appropriating 5000 dols. per annum to each State, because it believes that these additional funds will enable the Control Stations to increase their usefulness, and lighten, by the employment of an increased force, the labour which at certain seasons renders the chemist's work in the laboratory a very heavy and trying burden.

The publication of the method of analysis in all the minutiæ of detail goes far towards reducing differences, as it enables the chemists employed by the manufacturers to conform to it, as that the official analyses ought to be only confirmations of those previously obtained by the manufacturer. I am sure the trade will think the millennium has arrived if the discrepancies are once reduced to three-tenths of 1 per cent, and from the results laid before this meeting by the several committees it would seem as if that day is near at hand.

Permit me in conclusion to thank you for the interest you take in, and the unpaid labour you bestow upon, those investigations which in the end tend to benefit not only science but the fertiliser industry likewise, and to tender you also, on behalf of the committee on legislation and of the Association, their grateful appreciation of the consideration you accord to our representatives and requests.

In reply Professors Stubbs and Lupton spoke strongly against the Association taking part in any national legislation. They were willing to do everything possible with their State legislatures, but could not feel justified in sanctioning national interference in the matter.

After some further remarks from other members of the Association, on motion of Dr. Jenkins the communication of Mr. de Ghequier was referred to the Committee on Uniformity in Legislation.

The Committee on Revision of the Constitution, with a view to enlarging the field of the Association, was then asked to report, and submitted the following, which was unanimously adopted:—

The committee appointed to revise the constitution, in

accordance with the suggestions referred to it, recommends the following changes:—

Section 1 to read:

(1) This Association shall be known as the Association of Official Agricultural Chemists of the United States. The objects shall be (1) to secure uniformity and accuracy in the methods, results, and modes of statements of analysis of fertilisers, soils, cattle foods, dairy products, and other materials connected with agricultural industry; (2) to afford opportunity for the discussion of matters of interest to agricultural chemists.

Section 2 to read:

(2) Analytical chemists connected with departments of agriculture, agricultural experiment stations, agricultural colleges, State boards of agriculture, and other bodies charged with official control of the materials named in Section 1, shall alone be eligible to membership, and one such representative for each of these institutions or boards when properly accredited shall be entitled to a vote in the Association. Only such chemists as are connected with institutions exercising official fertiliser control shall vote on questions involving methods of analysing fertilisers. Any person eligible to membership may become a member at any meeting of the Association by presenting proper credentials and signing this constitution. All analytical chemists and others interested in the objects of the Association may attend its meetings and take part in its discussions, but shall have no vote in the Association.

Section 4 to read:

Strike out the word "three" in first line. Insert after "Committee on Nitrogen" the following:—"The committee on cattle foods and the committee on dairy products, whose reports shall be taken up, discussed, and disposed of in the order named. Additional committees may be appointed from time to time as the Association may direct.

Section 7 to read:

Seven enrolled members, entitled to vote, shall constitute a quorum for the transaction of business, instead of a "majority shall constitute a quorum."

Section 9 to be added:

All proposed alterations or amendments to this constitution shall be referred to a select committee of three at a regular meeting, and after report from such committee may be adopted by a vote of two-thirds of the members present and entitled to vote.

The remaining portions of the constitution, as now printed, to be retained unchanged.

Respectfully submitted,

H. C. White, Chairman.
E. H. Jenkins.
Wm. McMurtrie.

Dr. White reported as follows:—

The Committee on Phosphoric Acid has carefully considered the several suggestions referred to it, and respectfully recommends the following as the detailed method to be employed for the next year:—

*Method of Determining Phosphoric Acid in Fertilisers.*

(1) *Preparation of Sample.*—The sample should be well intermixed and properly prepared, so that separate portions shall accurately represent the substance under examination without loss or gain of moisture.

(2) *Determination of Moisture.*—(*a*) In potash salts, nitrate of soda, and sulphate of ammonia, heat 1 to 5 grms. at 130° C. till the weight is constant, and reckon water from the loss. (*b*) In all other fertilisers, heat 2 grms., or if the sample is too coarse to secure uniform lots of 2 grms. each, 5 grms. for five hours at 100° in a steam bath.

(3) *Water-soluble Phosphoric Acid.*—Bring 2 grms. on a filter; add a little water; let it run out before adding more water, and repeat this treatment cautiously until no phosphate is likely to precipitate in the filter. If the washings show turbidity after passing the filter, clear up with acid. When the substance is nearly washed in this manner, it is transferred to a mortar and rubbed with a rubber-tipped pestle to a homogeneous paste (but not further pulverised), then returned to the filter and washed with water until the filtrate measures not less than 250 c.c.; mix the washings. Take an aliquot (usually corresponding to $\frac{1}{4}$ or $\frac{1}{2}$ grm. of the substance), and determine phosphoric acid as under total phosphoric acid.

(4) *Citrate-insoluble Phosphoric Acid.*—Wash the residue of the treatment with water, into 150 c.c. flask with 100 c.c. of strictly neutral ammonium citrate solution of 1·09 density; shred and add the filter-paper; cork the flask securely; place in a water-bath with constant temperature of 65° C., and digest for thirty minutes at this temperature with frequent shaking. Filter the warm solution quickly, and wash with water of ordinary temperature.

Transfer the filter and its contents to a capsule. Ignite until the organic matter is destroyed; treat with 10—15 c.c. of concentrated hydrochloric acid; digest over a low flame until the phosphate is dissolved; dilute to 200 c.c.; mix; pass through a dry filter; take an aliquot and determine phosphoric acid as under total.

In case a determination of citrate-insoluble phosphoric acid is required in non-acidulated goods, it is to be made by treating 2 grms. of the phosphatic material without previous washing with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, &c.) the residue insoluble in ammonium citrate is to be digested with HCl and $KClO_3$ as described below.

(5) *Total Phosphoric Acid.*—Weigh 2 grms. into a flask or beaker; add 30 c.c. concentrated hydrochloric acid; heat and add cautiously and in small quantities at a time, about 0·5 grm. finely-powdered potassium chlorate. Digest at a gentle heat until all phosphates are dissolved and all organic matter destroyed; dilute to 200 c.c.; mix; pass through a dry filter; take 50 c.c. of filtrate; neutralise with ammonia; add about 15 grms. dry ammonium nitrate, and to the hot solution, for every decigrm. of $P_2O_5$ that is present, 50 c.c. of molybdic solution. Digest at about 65° C. for one hour; filter and wash with ammonium nitrate solution. (Test the filtrate by renewed digestion and addition of more molybdic solution.)

Dissolve the precipitate on the filter with ammonia and hot water, and wash into a beaker to a bulk of not more than 100 c.c. Nearly neutralise with hydrochloric acid; cool, and add magnesia mixture from a burette, slowly (one drop per second), stirring vigorously. After fifteen minutes add 30 c.c. of ammonia solution of density 0·95. Let stand several hours (two hours is usually enough). Filter; wash with dilute ammonia; ignite intensely for ten minutes and weigh.

(5) *Citrate-soluble Phosphoric Acid.*—The sum of the water-soluble and citrate-insoluble subtracted from the total gives the citrate-soluble.

*Preparation of Reagents.*

(1) *To prepare Ammonium Citrate Solution.*—Mix 370 grms. of commercial citric acid with 1500 c.c. of water; nearly neutralise with crushed commercial carbonate of ammonia; heat to expel the carbonic acid: cool; add ammonia until exactly neutral (testing by saturated alcoholic solution of coralline), and bring to volume of 2 litres. Test the gravity (which should be 1·09 at 20°) before using.

(2) *To prepare Molybdic Solution.*—Dissolve 100 grms. of molybdic acid in 400 grms., or 417 c.c., of ammonia of sp. gr. 0·96, and pour the solution thus obtained into 1500 grms., or 1250 c.c., of nitric acid of sp. gr. 1·20. Keep the mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phospho-molybdate. Decant the solution from any sediment, and preserve in glass-stoppered vessels.

(3) *To prepare Ammonium Nitrate Solution.*—Dissolve

200 grms. of commercial ammonium nitrate in water, and bring to a volume of 2 litres.

(4) *To prepare Magnesia Mixture.*—Dissolve 22 grms. of recently ignited calcined magnesia in dilute hydrochloric acid, avoiding excess of the latter. Add a little calcined magnesia in excess, and boil a few minutes to precipitate iron, alumina, and phosphoric acid; filter; add 280 grms. of ammonium chloride, 700 c.c. of ammonia of sp. gr. 0·96, and water enough to make the volume of 2 litres. Instead of the solution of 22 grms. of calcined magnesia, 110 grms. of crystallised magnesium chloride ($MgCl_2.6H_2O$) may be used.

(5) *Dilute Ammonia for Washing.*—One vol. ammonia of sp. gr. 0·96 mixed with 3 volumes of water, or, usually, 1 volume of concentrated ammonia with 6 volumes of water.

Respectfully submitted.

H. C. White, Chairman.
E. H. Jenkins,
W. C. Stubbs.

On motion of Prof. Lupton this was made the official method for the ensuing year.

(To be continued.)

## NOTICES OF BOOKS.

*On the Comparative Value of Nitrogen and Ammonia Salts.* By Thos. Brown. 1886.

The author of this paper, which was read at the Chemical Manure Manufacturers' Association, has been experimenting on various fertilisers for some years, and now brings forward the results of some of his experiments, hoping they may prove interesting and useful. Twenty years ago Mr. Brown first tried ammonium sulphate as a corn manure in Norfolk, the expense being less than that of sodium nitrate, which had been used very successfully, but the farmers who used it reported unfavourably; in this case it was used as a top dressing, but after it had been properly covered by the soil very satisfactory results were obtained, better even than those obtained with sodium nitrate.

In the spring of 1880 Mr. Brown again tried ammonium sulphate as a top dressing, but was surprised and disappointed at not finding any advantage from its use. His conclusions were:—1st, that ammonium sulphate has much less value than sodium nitrate when used as a top dressing; but, 2nd, it is a very useful manure when sown early with spring corn. In some experiments with root crops the results have generally been in favour of the ammonium sulphate. In 1873 18 tons 17 cwt. of swedes were obtained with 1½ cwt of sulphate per acre, and 17 tons 15 cwt. with 2 cwt. of nitrate per acre, the ammoniacal salt having an advantage of 1 ton 2 cwt. In 1875 the results were again in favour of the sulphate. Every year it is noticed that the sulphate and superphosphate plot gives a slight increase; by the addition of potash, however, the yield of the nitrate is brought slightly above that of the sulphate plot.

Other experiments were made with various soils to ascertain which one had more tendency to lose nitrogen than another. The samples were all placed in shallow boxes and ammonium sulphate sprinkled on the surface and raked in. The surface was damped every day and the boxes exposed to free air, but protected from the sun. After standing for twelve days the nitrogen was estimated and was found to have decreased in every case, in quantities varying from 23·3 per cent to 61·2 per cent of that added as ammoniacal salt. The greatest loss occurred in soils containing a high percentage of chalk.

The results recorded in this paper are of undoubted interest, and should point out to farmers the unadvisability of using costly manures containing nitrogen without consulting an expert who could advise them as to what was most suited to any particular kind of soil.

*Thomson's Conspectus, adapted to the British Pharmacopœia of* 1885. Edited by Nestor Tirard, M.D., F.R.C.P. New Edition. London: Longmans, Green, and Co.

This work opens with an Introduction giving a general description of the classes of bodies mentioned in the Pharmacopœia. Then follows the Conspectus strictly speaking, the various drugs and compounds being arranged in alphabetical order, with mention under each of its source (if needful), its composition, chemical and physical properties, action on the human system, its uses, doses, tests for its presence or for possible impurities, the substances with which it is incompatible, and an enumeration of the official preparations in which it occurs.

In the first item we note an oversight. Gum acacia is said to be composed of carbon, hydrogen, oxygen, *nitrogen*, and calcium. Nitrogen certainly does not enter into its composition.

The Appendix contains notices of some of the more important non-official medicines and preparations.

Then follows a chapter on poisons. Here we miss some old acquaintances, such as aniline, nitrobenzol, and the soluble compounds of chromium. The author says indeed:—"Many poisonous substances are purposely not noticed, because they are not likely to be employed as such, and consequently they do not demand general attention." Now the three substances just mentioned are not very likely to be used by a would-be suicide, nor yet to be intentionally administered by a poisoner. But they are all now prepared on the large scale, and they may be accidentally introduced into the system by various channels. The vapours of aniline and nitrobenzol, and the dust of the alkaline chromates, may be inhaled. Hence it is, we would submit, desirable that medical men, in the manufacturing districts at least, should be able to refresh their memories concerning the symptoms occasioned by these bodies and the treatment to be adopted.

In the directions for detecting cantharides the author lays some weight on the "green shining particles" found in matter extracted by means of the stomach-pump, or found, on a post-mortem examination, adhering to the coats of the intestine. These particles when found are decisive, but there are several other kindred insects (such as *Cantharis vittata*) met with in commerce which possess the same properties, and may be used for the same purposes, but which have not this colour.

The test here recommended for the detection of poisonous fungi, *viz.*, applying a piece of silver to the cut surface, is not fully trustworthy.

A third Appendix deals with the art of prescribing; a fourth states the proportions of the more active ingredients contained in pharmacopœial proportions; a fifth gives the atomic weights of the elementary bodies mentioned in the Pharmacopœia; a sixth gives a comparison of weights and measures; whilst a seventh gives the composition of the chief mineral waters, referred in some cases to a gallon, in others to 1000 grains, but in the majority of instances to a quantity of 7680 grains.

Concerning the utility of this little book there can be no doubt, and we hope that the trifling flaws which we have been compelled to point out may be eliminated in the next edition.

## CORRESPONDENCE.

### ON THE COMPOSITION OF HYDRATED SALTS.

*To the Editor of the Chemical News.*

Sir,—Messrs. S. Pickering and P. G. Sanford say, in their last letter, "Our point is a very simple one, and, if controvertible, can be controverted by experiment only," I join issue with them on this ground, and I ask—

1st. Have Messrs. S. Pickering and P. G. Sanford taken the trouble to prepare their alum from *pure* $Al_2O_3$ and KO? No, since they say "of ordinary crystallised alum"; *ordinary*, that is not *pure* as everybody knows.

2nd. Have these gentlemen designed to dry their *ordinary* alum according to my method, by means of a large mass of thoroughly desiccated alum? No; they dried it in the ordinary manner with sulphuric acid, and have taken no notice whatever of my last note, in which I stated that, when under the desiccator, alum loses water continuously for 167 days without *ever* remaining in the condition corresponding to 24 HO.*

3rd. Can these gentlemen deny the existence of $SO_3MgO=60$ united with 60 of water, that is 6·67 HO? Let them dry this salt with a large mass of the same salt deprived of nearly all its water, and they will obtain *equal weights*.

4th. Let them have the kindness to try the same experiment with CaCl, and they will find $CaCl=55·5$ united with 55 5 of water, that is 6·17 HO.

5th. May I ask my two honourable *confrères* to give a little attention to my theory? If they will, they will find that the "equal weights," which is the starting point of it, will soon become as familiar to them as the origin of the weights 5 : 3—3 : 1, &c., and they will not be long in recognising the application of these consequences to the whole science of chemistry *without any exception*. — I am, &c.,

E. Maumené.

Paris, January 15, 1887.

## CHROMIC ACID COMBUSTION OF GLYCERIN.

*To the Editor of the Chemical News.*

Sir,—I see in Chemical News, vol. lv., p. 2, that Messrs. Cross and Bevan state, in a short note, that they intend to apply the chromic acid combustion method to the analysis of carbon compounds. If they will turn to Chemical News, vol. liii., p. 271, they will see that I then applied chromic acid in the determination of carbon in waters, and checked the results by testing the method of combustion thus applied by means of known weights of pure cane-sugar, and obtained almost absolutely the theoretical amount of carbon in the sugar. Messrs. Cross and Bevan, therefore, have been anticipated by me, and, in fact, I began to use this method of combustion in August, 1884.

On the 7th of December, 1886, I read a paper before the Manchester Literary and Philosophical Society, further developing this method in the analysis of waters. I there pointed out how to determine the carbon, 1st, by the method given in my first paper; 2nd, by boiling with a solution of chromic acid of known strength and titrating the chromic acid still remaining unreduced by the carbon and hydrogen, by means of a standard ferrous sulphate solution, using a weak solution of potassium ferricyanide as an indicator.

I further pointed out that on boiling waters with chromic acid and sulphuric acid, the nitrogenous matter is *entirely* converted into ammonia, and this remains in the apparatus as ammonium sulphate. On distilling this off with pure caustic soda solution into a cylinder the distillate contains all the nitrogen (present in the water) as ammonia, and its amount is determined either by Nessler's reagent or in some other way.

I checked these analyses by testing the action of chromic acid on strychnine, obtaining fairly good results so far as the carbon and nitrogen were concerned. In the discussion which arose I pointed out the convenience of the method in *the ultimate analysis of organic compounds*, and reserved to myself the working out of the method, as then stated, for the determination of carbon, hydrogen, nitrogen, &c., in organic compounds of all kinds. I reserve that right now. My paper was really a preliminary note, and is not yet out of the printer's hands.

I intend to test my method of volumetric analysis of organic compounds thoroughly, and also ascertain how far chromic acid will be of service in the determination of nitrogen in manures, soils, foods, waters, and all kinds of organic compounds.—I am, &c.,

Charles A. Burghardt.

The Owens College, Manchester,
Jan. 11, 1887.

## HEATING APPARATUS.

*To the Editor of the Chemical News.*

Sir,—I have received from Prof. Dunnington, of the University of Virginia, a communication enclosing a description of a heating apparatus published by him in the *American Chemical Journal* for 1882. This apparatus, though it is not, in its details, adapted for the work for which the apparatus described in Chemical News, vol. liv., p. 302, was designed, yet embodies all its essential characters. I had not seen the paper he refers me to, and indeed the outward arrangement of the two forms of the apparatus differs so much that, had I done so, I should probably have overlooked the resemblance between them. With your permission I therefore gladly take the first opportunity to acknowledge the priority of Prof. Dunnington, and to thank him for his courtesy in drawing my attention to his paper.—I am, &c.,

G. H. Bailey.

The Owens College, Manchester,
Jan. 14, 1887.

## NICKEL LABORATORY UTENSILS.

*To the Editor of the Chemical News.*

Sir,—Like Mr. Blount, I have not been very fortunate in my use of nickel vessels, and as my experience has been in a different line from his it may be useful to give the results of it.

Tempted by the low price of these vessels, I procured two small dishes for milk analysis and used them several times. However, though they were never ignited (being used only for total solids and fat), they *lost weight every time*, the average loss being, for one vessel 2·8 m.grms., and for the other 3·1 m.grms., or a total loss of 0·051 grm. and 0·056 grm. respectively, after being used eighteen times each.

The loss, however, was not uniform, and as it amounted to 6 and 8 m.grms. on two occasions after use with buttermilk, I concluded it was due to the action of lactic acid.

To test this I weighed one of the dishes and evaporated a very dilute solution of the acid in it on the water-bath. As the result I found that the drop of strong acid left behind was coloured green, and that the dish had lost 6·5 m.grms in weight.

Thus, it is not safe to use these vessels for milk analysis unless the weight is checked before each determination. —I am, &c.,

Thomas Farrington, M.A., F.C.S.,
Analyst to the County Cork Agricultural Society.

Analytical Laboratory, 4, Waterloo Place,
Cork, Jan. 11, 1887.

**Detection of Salicylic Acid in Foods.**—H. Taffe. —The author agitates the suspected sample with a mixture of equal parts of ethylic ether and of petroleum ether. The salicylic acid is thus dissolved out even when in very small quantities.—*Bull. de la Soc. Chim. de Paris*, vol. xlvi., No. 12.

* Pure alum, octahedric or cubic, remains quite transparent with 28·73 HO; but when it is put under a shade with sulphuric acid, in two hours time it shows opaque spots, the number of which increase incessantly, and, I repeat it, without stopping, to 26, 25, 24, . . . . 7, 6, 5, HO, &c.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Moniteur Scientifique, Quesneville.*
3rd Series. Vol. xvi., November, 1886.

A Presidential Address delivered before the Chemical Section of the British Association.—W. Crookes, F.R.S.—From the Chemical News.

On the Methods of Chemical Fractionation.—W. Crookes, F.R.S.—From the Chemical News.

The Fractionation of Yttria.—W. Crookes, F.R.S.—From the Chemical News.

Studies on Melitose or Raffinose extracted from Treacle, Cotton-Seed, and from the Eucalyptus-Manna.—B. Tollens and P. Rischbiet —From *Liebig's Annalen*, and already noticed.

Sanitary Value of the Chemical Analysis of Potable Waters.—Dr. W. G. Tucker.—From the Chemical News.

Arificial Production of Codeine.—From the *Pharmaceutical Journal.*

Optical Method for the Analysis of Quinine Sulphate.—D. Hooper, F.C.S.—From the *Pharmaceutical Journal.*

Poassium and Sodium Peroxides: A Lecture Experiment.—H. Carrington Bolton.—From the Chemical News.

Method for Determining the ill-tasting Oil in Alcohol, especially in Brandy and Liqueurs.—Dr. J. Traube.—From the Chemical News.

December, 1886.

Petroleum and its Products (conclusion). — Mr. Boverton Redwood.—From the *Journal of the Society of Arts.*

Study of the Theory of Turkey-Red Dyeing.—P. Lukianoff.—Alizarine oils consist of two matters, the one sort soluble in water and the other insoluble. The soluble matter has a very distinct acid character, whilst the insoluble portion contains no sulphur, and contains glycerides. The author has sought to determine what part is played respectively by the soluble and the insoluble matter in the formation of the red lake. To determine this point he took five swatches of cotton and prepared them, one with the soluble portion alone, another with the insoluble portion alone, and the remaining three with mixtures of the two in different proportions. The swatches after oiling were submitted to the usual treatments and lastly dried and brightened. The swatch oiled with the soluble portion alone afforded the purest and reddest tone, but it was relatively the least full and level. The swatch prepared with the insoluble portion alone was the fullest in colour and the most even, but its tone was impure and yellowish. The other swatches presented intermediate degrees of brightness and of saturation, according to the proportions of the two ingredients used. The swatches oiled with the insoluble portion were the best able to resist the action of boiling soap-lyes and of chlorine.

Chrome Mordants in Dyeing Logwood Blacks on Wool.—J. B. Wilkinson.—From the *Journal of the Society of Dyers and Colourists.*

Industrial Review and Patents :—

Obtaining metallic copper, zinc, lead, and silver, and lead peroxide by the electrolysis of their fluosilicates or fluoborates.—G. Leuchs.

Electrolytic treatment of lead and argentiferous copper ores.—E. Marchese.

Process for separating and re-collecting the fatty acids carried away by residual water.—C. E. Schroers.

Improvement in the separation and purification of the grease of suint and of its combination with water to form a waxy substance known as lanoline.—Fabrik Chemischer Producte, Berlin.

Purification of the grease of suint.—W. Graff.

Preparation of neutral and supersaturated soaps by adding to ordinary soaps ammonium sulpholeate, or sulpholeic acid.—Dr. W. Kirchmann.

Assay of Various Primary Materials used in Dyeing and Printing. — Brief directions for examining samples of alizarine, starch, sodium bichromate, cake-alum, red liquor, glycerin, and antimonial mordants. (*Dingler's Journal*).

On Soaps.—C. R. Alder Wright and C. Thompson.—From the *Journal Soc. Chem. Indust.*

Chrome Mordants in Dyeing.—Emile Blondel.—The author reviews the various methods which have been proposed for fixing chrome upon the vegetable fibre. He describes the alkaline chrome mordant of Kœchlin as modified by himself, the basic nitrate and a double chromium calcium, or chromium magnesium nitrate. The latter serves well for fixing sumac, bark, catechu, berries, gallocyanine, anthracene blue, cœruleine, &c. On oiled tissues the shades obtained are more intense.

Industrial Society of Mulhouse.—Session of the Chemical Committee, Oct. 13, 1886.—M. Grosheintz sent in a paper on a thermometer for measuring the mean temperature of a hot flue and transmitting its indications direct to the furnace-room.

A sealed paper deposited by M. Rud. Geigy (Nov. 12, 1885) was opened at his request. It contained the following process for a blue dye for cottons. If we diazotise a mol. of diamido-diphenetol and pour the solution of the diazo-derivative into the solution of 2 mols. of *a*-naphthol sulphonic acid (prepared with diazo-naphthionic acid) we obtain a blue colouring matter which dyes cotton a blue without mordant either in an acid or an alkaline bath. The colour bears acids and soaping.

M. Noelting presented a memoir on the azimido-derivatives.

Determination of Indigo on Textile Fibres.—Adolphe Renard.—The author takes 10 grm. of the dyed material, introduces them into a flask with 200 c.c. of a solution of neutral sodium hydrosulphite mixed with milk of lime. The solution is prepared by adding 2 litres water and 100 c.c. milk of lime to 100 c.c. of neutral sodium hydrosulphite prepared with sodium bisulphite at 35° B. The mixture is heated to 60—70° in the water-bath, when the fibres are decolourised, and, as well as the liquid, take a yellowish colour. A current of coal-gas is then passed into the flask, which is agitated until every trace of blue colour has disappeared; the liquid is then quickly decanted into a graduated jar, still continuing the current of gas. When cold, he measures the volume of the liquid and precipitates with hydrochloric acid, and after settling for twelve hours he receives the deposit of indigotine upon a small filter. It is washed, dried, dissolved in 10 c.c. of fuming sulphuric acid, and determined by Müller's method.

Use of Ammonium Citrate in the Analysis of Precipitated Phosphate.—H. Shepherd.—From the Chemical News.

Determination of Mixtures of Milk and Cane-Sugar.—Stokes and Bodmer.—From the Chemical News.

Determination of Milk-Sugar in Milk.—Creydt and Tollens.—From the Chemical News.

Use of Acetic Acid in the Analysis of Milk.—Johnstone.—From the Chemical News.

## MISCELLANEOUS.

**Normal School of Science and Royal School of Mines.**—We are requested to state that the number of applications for admission to the Normal School of Science and Royal School of Mines, at South Kensington, at the commencement of the present Session, having been considerably in excess of the accommodation which the School can afford, it has become necessary to adopt some process of selection for the future. Hereafter, application for admission should be sent to the Registrar of the School before the end of May, accompanied by a statement of the studies which the applicant has already pursued, the examinations he has passed, and the name of a teacher (or teachers) to whom reference may be made. Such applications will be considered by the Dean and Council of the School, who will decide on them according to their merits. A knowledge of Elementary Mathematics, such as is required of all Royal Exhibitioners and National Scholars, will be held to be of the first importance for those who desire admission to the Course for the Associateship of the School; while for occasional students, who propose only to take up certain specific branches of Science, some preliminary knowledge of them will have weight.

**Chemistry of the Alkaloids and Albumenoids.**—We are requested to announce that Prof. Armstrong's Course of twenty lectures on the Chemistry of Nitrogen and its Compounds, with special reference to the recent investigations of the Alkaloids, Albumenoids, &c., to be delivered at the City and Guilds of London Institute, Central Institution, Exhibition Road, S.W., on Mondays and Wednesdays, at 5 p.m., will commence on Monday, January 24th, and not on the 27th as advertised in some papers. The following notes are extracted from the Syllabus of the Course:—"Inasmuch as nitrogen compounds are essential constituents of all animal and vegetable structures, and as the characteristic properties of the nitrogenous compounds are, it is to be supposed, largely conditioned by the presence of nitrogen as dominant element, the study of the chemistry of nitrogen is of the highest importance. To mention but a few cases:—It is of importance in relation to the question of the comparative values of *different food-stuffs*, and in relation to the use of *nitrogenous manures*. It is of importance in relation to the phenomena of *fermentation*, and therefore to the *brewing* industry. It is of importance in relation to the putrefactive changes induced by the *disease-producing bacteria*, and also to the physiological and medicinal effects produced by alkaloids. It is of importance in relation to the *tanning, wool and silk dyeing industries*, as the raw materials dealt with are nitrogenous compounds. In the lectures the endeavour will be made first to clearly bring out and illustrate the characteristics of the element nitrogen by reference to the properties of its simpler compounds. Subsequently an account will be given of the methods adopted in investigating the alkaloids, albumenoids, &c., and of the state of our knowledge of the more important nitrogen compounds. Whenever possible experimental illustrations will be given of the operations and methods described.

Amongst the most recent applications of the Æolus Waterspray system of heating, cooling, and ventilating, are the Conservative Club, Birmingham; Castle Street Schools, Bristol; Heath Town Chapel, Wolverhampton; Four Courts, Dublin; Mission Hall, Brondesbury; St. Peter's Church, Jarrow-on-Tyne; Parish School Room, York; Mr. Mendelssohn's Studios, Cathcart Road, South Kensington; large theatre of the Polytechnic, Regent Street; The London and Provincial Turkish Bath Co., 76, Jermyn Street; St. Mary's Schools, Gibbet Street, Halifax; H.M. Prison, Bodmin; offices of the Rio Tinto Co. (fourth installation); All Saints Church, Highgate; Congregational Church, Rectory Road, Stoke Newington; Western Daily Press Office, Bristol (second installation),

## MEETINGS FOR THE WEEK.

Monday, 24th.—London Institution, 5.
—— Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "The Diseases of Plants," by Dr. Thudichum.
Tuesday, 25th.—Institution of Civil Engineers 8.
—— Royal Medical and Chirurgical, 8.30.
—— Royal Institution, 3. "Function of Respiration," by Prof. Arthur Gamgee, F.R.S.
—— Society of Arts, 8 "The Volcanic Eruption in New Zealand," by J. H. Kerry Nicholls, F.R.G.S.
Wednesday, 26th.—Geological, 8.
—— Society of Arts, 8. "Photographic Lenses," by J. Traill Taylor.
Thursday, 27th.—Royal, 4.30.
—— London Institution, 6.
—— Telegraph Engineers, 8.
—— Royal Institution, 3. "Molecular Forces," by Prof. A. W. Rücker, F.R.S.
Friday, 29th.—Royal Institution, 9. "The Lineal Eye in Lizards," by W. Baldwin Spencer, M.A.
—— Quekett Club, 8.
Saturday 29th.—Royal Institution, 3. "Modern Composers of Classical Song—Robert Franz," by Carl Armbruster.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THE CHEMICAL NEWS.

Vol. LV. No. 1418.

## THE DETECTION OF ADULTERATION OF METALLIC NICKEL AND OTHER METALS BY THE MAGNET.

By THOMAS T. P. BRUCE WARREN.

During the winter of 1881-2, whilst lecturing to a class at the Silvertown Institution, on Electricity and Magnetism, I was desirous of showing to the students the magnetic property of metallic nickel. Through the kindness of Matthew Gray, Esq., at that time President of the Institution, I borrowed from the India-rubber, Gutta-percha, and Telegraph Co., Silvertown, a specimen of nickel cubes, which consisted in fact of two samples received some time before from Germany. The difference in price of the two samples was so little that they were thrown together into a drawer, as it was thought at the time that there could not be much difference between them with respect to purity, &c.

A handful of these cubes was placed on the table, and, on bringing an ordinary compound horse-shoe magnet near the cubes, I was very much surprised to find that, whilst some of these cubes were forcibly attracted by the magnet, others were not affected at all, or so slightly that they could not be supported by the magnet against their own gravity. Some cubes were attracted slightly when placed very near to the magnet, but could not be lifted.

I thought the matter of sufficient interest that I entrusted the chemical examination of these samples to one of the students in the Laboratory of the Institution.

I afterwards examined the whole of the nickel contained in the drawer with the magnet in the same way, and in two or three minutes I had the samples sorted out into their original lots of 2 kilogrammes each.

The magnet readily picked out the better quality at the rate of twenty or thirty cubes at a time, until what was left could not be drawn out by the magnet. To make sure of the result, the "magnetically selected" cubes were again tested with the magnet, when it was found that a few non-magnetic cubes had been drawn up by entanglement with the others. By the second operation the separation was perfect.

There was no very marked difference in these cubes which would lead one to suspect anything worth noting. A closer examination showed that the non-magnetic cubes were a trifle whiter and presented the absence of a striated structure, which was well defined, though unequally, with the magnetic cubes.

This method of examination was extended to samples of English grain nickel, and also to portions of anodes of English, American, and German manufacture.

It may be sufficient to remark here that the grain nickel was powerfully attracted, and that the anodes, although drawn up by the magnet, were not so strongly attracted as the grain or magnetic cubes.

The fact that nickel has become an article of commercial importance, and that chemical analysis has disclosed the fact that this metal is liable to extensive adulteration, which can be so easily detected by the magnet, led me to believe that this subject deserved a more extended examination.

Special examinations of these cubes were made for lead, bismuth, antimony, cobalt, and sulphur, which were decidedly absent, although traces of some of these were detected in the anodes.

The following gives the percentage of composition of the cubes referred to;—

| | Magnetic. | Non-magnetic. |
|---|---|---|
| Copper .. .. | 0·083 | 33·779 |
| Carbon .. .. | 0·071 | 0·365 |
| Silica .. .. .. | 0·409 | 0·160 |
| Iron .. .. .. | 2·457 | 0·841 |
| Arsenic .. .. | 0·117 | 0·865 |
| Tin .. .. .. | 0·749 | 0·461 |
| Nickel .. .. | 96·670 | 63·690 |
| | 100·556 | 100·161 |

The oxide of nickel obtained from the non-magnetic sample was reduced by heating in a current of hydrogen: this reduced metal was then even more magnetic than the other sample. A portion was placed in a test-tube, which was inserted between the poles of a powerful horse-shoe magnet; it readily took up an axial position, which was not disturbed on carefully rotating the tube.

Portions of this metal were alloyed with small quantities of tin, arsenic, and antimony separately, which had a decided effect on its magnetic property.

Cobalt in its pure state behaves like nickel, and when alloyed with paramagnetic metals is similarly affected.

I have extended the examination more recently to nickel crucibles and dishes, and also to the wire triangles before and after heating, all of which are magnetic both before and after heating.

I have frequently noticed that the loss on one of these crucibles, when strongly heated over a Bunsen burner, is very slight compared with the bulky accumulation of black deposit which is produced. A few days ago I collected considerably over a gramme of this powder, which on analysis consisted almost entirely of graphitoidal carbon, with minute quantities of nickel, iron, and silica.

I may mention that a platinum crucible heated in the same flame remained quite bright: the curious deduction arising from this is, that these vessels are capable of actually decomposing the gas in a Bunsen's flame. A precaution which should therefore be taken is *not* to use these supports for platinum crucibles.

This unlooked-for result led me to use hydrogen as a means of heating these nickel crucibles, taking care, of course, that the intense heat was not allowed to act injuriously on them. If coal-gas be used, the flame must not be allowed to impinge upon the crucible.

I have now some experiments in hand with a view of ascertaining their behaviour in a muffle furnace heated with ordinary gas, as alkaline fusions for the analysis of earthy minerals are frequently required in practice.

So far as my experiments have gone the crucible gains in weight, due to oxidation when heated in a muffle, but there is this difference—that the oxide formed is strongly adherent to the crucible, and is not rubbed off by the fingers, in the hydrogen flame: oxidation does not take place on heating, but the precaution is necessary, to allow the cooling to go on in a current of this gas in order to avoid oxidation.

I find that there is a difference in the composition of the nickel gauze and wire supports, and the crucibles and dishes. Malleability, so far as my analyses go, is produced by the addition of iron and manganese.

The composition of the malleable alloy from which the dishes and crucibles are made will be given in my next paper on this subject.

I may just state that commercial manganese and some other metals which are generally classified as magnetic are met with, in which magnetic attraction is notoriously absent. This deserves attention, as in the construction of magnets other metals are added to iron to increase its retentive power when hardened, and it is by no means improbable that the polarity of soft iron may be modified as regards its residual magnetism by the addition of other metals of the same or opposite series.

## NICKEL CRUCIBLES.

By JOHN H. J. DAGGER, F.I.C.

Having, for the past fifteen months, used nickel crucibles in my laboratory, a few notes on my own experience with them may be of interest.

At first I found that unless care was taken to keep the metal from contact with the reducing zone of the flame the crucible became covered with black flakes which, on cooling, scaled off, seriously affecting the weight of the crucible.

I then made the following experiments.

A clean polished lid was weighed and then heated over an ordinary Bunsen flame turned down and screened from all draughts, the lid so being exposed to the upper point of the reducing zone of a small flame. After heating for an hour it was allowed to cool. On examination the lid was blackened and corroded in form of a small ring at the point where the flame impinged on the metal.

On weighing—

| | | |
|---|---|---|
| (1) | Weight of lid before ignition .. | 8·9310 grms. |
| | „ „ after „ .. | 8·9385 |
| | Gain . .. .. .. | 0·0075 |

The burner was then turned to a full flame so that the entire surface of the lid was exposed to the reducing zone. At the end of an hour a comparatively large amount of deposit had formed on the lid.

On weighing—

| | | |
|---|---|---|
| (2) | Weight of lid before ignition .. | 8·9385 grms. |
| | „ „ after „ .. | 9·0030 |
| | Gain.. .. .. .. | 0·0645 |

After cleaning and comparing with original weight of lid—

| | Grms. |
|---|---|
| Weight of clean polished lid before ignition.. | 8·9310 |
| After two ignitions .. .. .. .. .. .. | 8·9250 |
| Loss on original lid .. .. | 0·0060 |

The black deposit was then transferred to a weighed porcelain crucible and heated to redness with access of air till weight remained constant.

| | |
|---|---|
| Weight of residue.. .. | 0·0525 grms. |
| After ignition.. .. .. | 0·0090 |
| Loss . .. .. | 0·0435 |

The ignited residue was of a brownish grey colour and contained nickel, the loss being apparently carbon.

A second lid was then weighed and heated over the oxidising zone of a Fletcher Argand Bunsen, so that the whole surface became heated. At the end of an hour the under surface of the lid was slightly blackened, the upper being covered with a brownish film.

On weighing—

| | | |
|---|---|---|
| (1) | Weight before ignition .. | 7·9570 grms. |
| | „ after „ .. | 7·9610 |
| | Gain . .. .. | 0·0040 |

On re-heating for another hour and weighing—

| | | |
|---|---|---|
| (2) | Weight before ignition .. | 7·9610 grms. |
| | „ after „ .. | 7·9630 |
| | Gain .. .. | 0·0020 |

On lowering this lid into the reducing zone it became coated with the black deposit.

It follows from these experiments that nickel crucibles can be used if exposed to the oxidising zone only.

In course of an analysis a quantity of the mixed oxides of Sn and Sb were fused with caustic soda in a weighed crucible over a Fletcher Argand flame for twenty minutes. The crucible was afterwards cleaned and re-weighed.

| | |
|---|---|
| Before fusion . .. | 18·6165 grms. |
| After „ .. .. | 18·6145 |
| Loss .. | 0·0020 |

Fusion with nitre corroded the metal, giving a rough grey surface. The nitre showed traces of nickel.

I find that for fusions with alkalies at low red heat, and for evaporations of alkaline solutions, the crucibles are very satisfactory; at higher temperatures, small quantities of nickel pass into the fused matter.

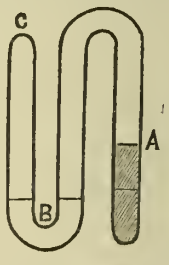
A nickel crucible, if carefully used, will last about sixty fusions; after that it begins to develop cracks. Nickel wire triangles I find to be unsatisfactory; after heating several times they become brittle and break suddenly.

3, West Bank Road, Edge Lane,
Liverpool, Jan. 14, 1887.

## ON THE DECOMPOSITION OF AMMONIUM CHLORIDE BY MEANS OF AN ALLOY OF ZINC AND IRON.

By H. N. WARREN, F.R.A., A.I.C.

Two grms. of finely-powdered zinc eisen (consisting of zinc alloyed with 12 per cent of iron) were intimately mixed with 4 grms. of pure dried ammonium chloride, and introduced into a pressure-tube constructed as in Fig. 1. In the limb A is introduced ammonium chloride mixed with the zinc compound, and in the bend B a small quantity of mercury, the point C being afterwards closed by means of the blowpipe. The limb A is maintained at a constant temperature by means of a chloride of zinc




bath. The reaction having terminated, the tube was allowed to cool, and the point C being first immersed under the surface of water was quickly broken, the mercury rushing out with great violence in consequence of a large quantity of compressed hydrogen contained in the tube, due to secondary actions, &c. The mercury in coming in contact with the water immediately swelled up to several times its original bulk, giving off large quantities of ammonia gas, and in every respect resembling the well-known ammonium amalgam; and shortly regaining its original size and fluidity. On experimenting a second time, using instead of mercury a fluid amalgam of tin and mercury, the amalgam was considerably more stable, even when under the surface of water. A third experiment was performed, substituting for the zinc pure lime, but on introducing the mercury into water no swelling of the mercury was observed. It would thus appear that the zinc compound in the first place frees from the ammonium chloride its ammonium, $H_4N$, the zinc combining with the chlorine according to the following equation, $2H_4NCl + Zn = ZnCl_2 + 2H_4N$; but the ammonium being an unstable compound or body, and not being able to exist at the ordinary normal pressure, is at once resolved into ammonia and hydrogen gas, as is the case when the above-mentioned experiments are not performed

under pressure; the reaction at the commencement in both cases being evidently identical, but in the latter case being confined and the pressure gradually becoming more intense, it exerts, as it were, an influence over the atoms to connect themselves somewhat more closely together, thus giving greater stability to the ammonium and at the same time inducing it to amalgamate with the mercury. In performing these experiments I may mention that great care is required by the experimenter, and in the method of constructing the pressure-tube, since a malformed tube may result in a serious explosion.

## ANALYSES OF COMMERCIAL FERTILISERS.

(Continued from p. 33.)

Dr. Gascoyne, from the Committee on Potash, then recommended the following method for determining potash:—

*Method for Determining Potash.*

In case the potash is contained in organic compounds like tobacco stems, cotton-seed, hulls, &c., it is to be saturated with strong sulphuric acid and ignited in a muffle to destroy organic matter. Pulverise the fertiliser (200 or 300 grms.) in a mortar; take 10 grms., boil for ten minutes with 200 c.c. water, and after cooling and without filtering, make up to 1000 c.c. and filter through a dry paper. If the sample have 10—15 per cent $K_2O$ (kainite), take 50 c.c. of the filtrate; if from 2—3 per cent $K_2O$ (ordinary potash fertilisers), take 100 c.c. of the filtrate. In each case make the volume up to 150 c.c., heat to 100°, and add, drop by drop, with constant stirring, slight excess of barium chloride; without filtering, in the same manner add barium hydrate in slight excess. Heat, filter, and wash until precipitate is free of chlorides. Add to filtrate 1 c.c. strong ammonium hydrate, and then a saturated solution of ammonium carbonate until excess of barium is precipitated. Heat. Add now in fine powder 0·5 grm. pure oxalic acid or 0·75 grm. ammonium oxalate. Filter, wash free of chlorides, evaporate filtrate to dryness in a platinum dish, and, holding dish with crucible tongs, ignite carefully over the free flame below red heat until all volatile matter is driven off.

The residue is now digested with hot water, filtered through a small filter, and washed with successive small portions of water until the filtrate amounts to 30 c.c. or more. To this filtrate, after adding two drops of strong hydrochloric acid, is added, in a porcelain dish 5—10 c.c. of a solution of 10 grms. of platinic chloride in 100 c.c. of water. The mixture is now evaporated on the water-bath to a thick syrup, or further, treated with strong alcohol, washed by decantation, collected in a Gooch crucible or other form of filter, washed with strong alcohol, afterwards with 5 c.c. of ether, dried for thirty minutes at 100° and weighed.

It is recommended that if there is an appearance of white foreign matter in the double salt it should be washed with 10 c.c. of a half-concentrated solution of $NH_4Cl$ which has been saturated by shaking with $K_2PtCl_6$, rejecting the first portion running through and using 10 c.c. of fresh solution, returning the latter portion five or six times upon the salt and finally using another portion, and then alcohol and ether, after the method recommended by Gladding.

As an alternative the entire method of Lindo, as modified by Gladding, may be used in the determination of potash when, in the opinion of the analyst, it is found satisfactory.

The use of the factor 0·33056 for converting $K_2PtCl_6$ to KCl and 0·19308 for converting $K_2O$ are continued.

Respectfully submitted,

W. J. Gascoyne, Chairman.
Clifford Richardson.
M. A. Scovell.

On the motion of Dr. White the recommendations were adopted as the official method for the ensuing year.

Dr. Gascoyne then presented the report of the Committee on Nitrogen, embracing recommendations for the use of the Ruffle method.

Professor Stubbs desired to know if, were this report adopted, the Ruffle method alone would be official, and this being apparently the case, he dissented from its adoption.

Dr. Jenkins said that he felt that he could not give up the Kjeldahl and absolute method, but that were the Ruffle adopted as official he should check his results by that.

Considerable opposition to the adoption of any one method being apparent, it was moved and passed—

That no single method be selected as official, but that the Association recognise as such either the Ruffle, Kjeldahl, absolute, or soda-lime methods, when carried out according to working details to be supplied by the committee.

These details are presented in the Appendix.

Miscellaneous business being in order, the Committee on a Uniform Law presented the following report:—

The committee appointed at the last annual session "to consider the question of uniformity of legislation and regulations as to the inspection of fertilisers, and to prepare a draft of uniform law," and to whom the communication of the National Fertiliser Association presented through Mr. de Ghequier has been referred, has taken these matters under consideration and begs leave to report:—

(1) The committee is of opinion that no recommendation concerning national legislation should be made by this Association.

(2) The committee recommends that the communication presented by Mr. de Ghequier be spread on the minutes.

(3) The conditions in the different States are so various that it is clearly impracticable to draft a uniform law covering the details of inspection, regulation of sale, &c., of commercial fertilisers that would be generally acceptable.

(4) With the legal and commercial features of such legislation this Association has nothing to do. The form of statement of the analysis of fertilisers is a matter, however, the discussion of which is clearly within our province. The committee suggests the following as a proper form in which guaranteed and official analyses should be expressed:—

| | Per cent. |
|---|---|
| Moisture | |
| Soluble phosphoric acid | |
| Reverted phosphoric acid | |
| Insoluble phosphoric acid | |
| Total available phosphoric acid | |
| Total phosphoric acid | |
| Nitrogen | |
| Equivalent to ammonia | |
| Potash ($K_2O$) | |

The committee further suggests that the same form, or such part or parts of it as may be necessary, be recommended as proper to be attached to bags or packages containing fertilisers.

And the committee recommends that each member of this Association use his influence to have a clause inserted in the fertiliser law of his State looking to the adoption of the forms of analysis above expressed.

Respectfully submitted,

H. C. White, Chairman.
P. E. Chazal.
E. H. Jenkins.

Professor Stubbs moved to strike out the words "total available" in the form recommended by the committee, which was carried, and the report was then adopted.

(To be continued.)

## A METHOD FOR THE SEPARATION OF SODIUM AND POTASSIUM FROM LITHIUM BY THE ACTION OF AMYL ALCOHOL ON THE CHLORIDES,

### With some Reference to a Similar Separation of the Same from Magnesium and Calcium.*

By F. A. GOOCH.

(Continued from page 30.)

Used simply to wash the precipitate, amyl alcohol cannot, of course, exert an effect at all comparable with that manifested in the experiments which have been described, but to know just what this action may be is important. Experiments (18) to (22) were undertaken, therefore, to elucidate this point.

Weighed amounts of the test solutions were evaporated nearly to saturation in small glass beakers amyl alcohol added, and, as in the previous experiments, the whole heated until the salt had deposited and the residual alcohol had boiled quietly for some minutes at its ordinary boiling point, the liquid decanted, filtered under gentle pressure by means of a weighed perforated crucible and felt of asbestos, the filtrate measured, the residue dislodged with the aid of a rubbing-rod and transferred to the crucible and washed with anhydrous amyl alcohol, the washings being collected and measured. The crucible and contents were dried over a free flame turned low so that the heat should not reach the melting-point of the chlorides.

These results show very plainly that the solvent effect of anhydrous amyl alcohol used for washing under the conditions described is trifling in the extreme, and may be neglected utterly providing the amount of the washing is not altogether disproportionate to the needs of the case.

We pass next to the consideration of the separation of

| | Weight of NaCl taken. | Weight of NaCl found. | Weight of NaCl found, corrected for solubility in residual amyl alcohol. | Error of corrected weight of NaCl found. | Volume of residual amyl alcohol. | Volume of amyl alcohol in washings. |
|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | C.m.³ | C.m.³ |
| (18) | 0·0947 | 0·0937 | 0·0947 | 0·0000 | 24 | 44 |
| (19) | 0·1080 | 0·1074 | 0·1082 | 0·0002+ | 19 | 53 |

| | Weight of KCl taken. | Weight of KCl found. | Weight of KCl found, corrected for solubility in residual amyl alcohol. | Error of corrected weight of KCl found. | Volume of residual amyl alcohol. | Volume of amyl alcohol in washings. |
|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | C.m.³ | C.m.³ |
| (20) | 0·1846 | 0·1837 | 0·1847 | 0·0001+ | 20 | 60 |
| (21) | 0·1964 | 0·1946 | 0·1961 | 0·0003− | 30 | 45 |
| (22) | 0·1857 | 0·1839 | 0·1854 | 0·0003− | 30 | 60 |

| | Weight of NaCl taken. | Weight of NaCl found. | Weight of NaCl found, corrected for solubility in amyl alcohol. | Error in weight of NaCl found. | Error in corrected weight of NaCl found. | Volume of amyl alcohol used. Residual. | Total. |
|---|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | Grm. | C.m.³ | C.m.³ |
| (23) | 0·1089 | 0·1092 | 0·1095 | 0·0003+ | 0·0006+ | 7 | 70 |
| (24) | 0·1084 | 0·1085 | 0·1090 | 0·0001+ | 0·0006+ | 12 | 80 |
| (25) | 0·1074 | 0·1067 | 0·1074 | 0·0007− | 0·0000 | 18 | 90 |

| | Weight of LiCl taken. | Weight of $Li_2SO_4$ found. | Weight of LiCl found. | Corrected weight of LiCl found. | Error in weight of LiCl found. | Error in corrected weight of LiCl found. |
|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | Grm. | Grm. |
| (23) | 0·1298 | 0·1682 | 0·1299 | 0·1296 | 0·0001+ | 0·0002− |
| (24) | 0·1227 | 0·1592 | 0·1230 | 0·1225 | 0·0003+ | 0·0002− |
| (25) | 0·0116 | — | — | — | — | — |

| | Weight of KCl taken. | Weight of KCl found. | Weight of KCl found, corrected for solubility in amyl alcohol. | Error in weight of KCl found. | Error in corrected weight of KCl found. | Volume of amyl alcohol used. Residual. | Total. |
|---|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | Grm. | C.m.³ | C.m.³ |
| (26) | 0·2051 | 0·2036 | 0·2053 | 0·0015− | 0·0002+ | 34 | 100 |
| (27) | 0·2022 | 0·2013 | 0·2032 | 0·0009− | 0·0010+ | 37 | 100 |
| (28) | 0·2109 | 0·2096 | 0·2104 | 0·0013− | 0·0005− | 16 | 100 |
| (29) | 0·0984 | 0·0970 | 0·0980 | 0·0014− | 0·0004− | 20 | 90 |

| | Weight of LiCl taken. | Weight of $Li_2SO_4$ found. | Weight of LiCl found. | Corrected weight of Li Cl found. | Error in weight of LiCl found. | Error in corrected weight of LiCl found. |
|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | Grm. | Grm. |
| (26) | 0·1256 | 0·1638 | 0·1265 | 0·1248 | 0·0009+ | 0·0008− |
| (27) | 0·1287 | 0·1677 | 0·1296 | 0·1277 | 0·0009+ | 0·0010− |
| (28) | 0·0113 | — | — | — | — | — |
| (29) | 0·0113 | — | — | — | — | — |

| | Weight of NaCl taken. | Weight of KCl taken. | Weight of NaCl+KCl found. | Corrected Weight of NaCl+KCl found. | Volume of Amyl Alcohol used. Residual. | Total. |
|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | C.m.³ | C.m.³ |
| (30) | 0·1053 | 0·1031 | 0·2064 | 0·2084 | 22 | 100 |
| (31) | 0·1051 | 0·0945 | 0·1988 | 0·2003 | 16 | 80 |

| | Weight of LiCl taken. | Error in Weight of NaCl+KCl found. | Error in corrected Weight of NaCl+KCl found. |
|---|---|---|---|
| | Grm. | Grm. | Grm. |
| (30) | 0·0113 | 0·0020− | 0·0000 |
| (31) | 0·0113 | 0·0008− | 0·0007+ |

* *Proceedings of the American Academy of Arts and Sciences*, 1886-1887.

the chlorides of sodium and potassium from lithium chloride. Weighed portions of the test solutions were concentrated and treated with amyl alcohol in the manner described until the precipitated salt was entirely free from water and the supernatant alcoholic solution of the lithium chloride boiled constantly at a point not far from that of the amyl alcohol employed. Then the liquid was cooled, a drop or two of strong hydrochloric acid added in accordance with the evident suggestion of the preliminary experiments previously mentioned, and heat again applied until the boiling had continued, as before, for some minutes at one point. The filtration, washing, drying, and weighing of the residue were effected as in experiments (18) to (22). In those of the experiments in which the lithium salt in solution was also determined, the end was accomplished by evaporating the filtrate and washings to dryness, treating the residue with sulphuric acid, and igniting and weighing as lithium sulphate. In the table (see p. 40) the weight of insoluble chloride actually found is given in one column, and this weight, corrected according to the data previously determined for the solubility of the chloride in the residual amyl alcohol appears in the column adjoining. So also the weight is given of the lithium sulphate actually found, and an adjacent column contains the result of correcting this weight for the accompanying sodium or potassium sulphate, or both, upon the hypothesis that these salts are neutral sulphates after the ignition. In the case of quantities so minute the error which is introduced by such an assumption cannot be considerable, and in relation to this point Dittmar* maintains that comparatively large amounts of acid sodium or potassium sulphate may be reduced to the neutral salt by ignition simply. The figures of the column showing the weights of lithium chloride found are derived by calculation from the weights of lithium sulphate actually found. The other headings of the table are sufficiently intelligible without further explanation.

It will be noticed that in experiments (23), (24), (26), and (27), the corrected error in the weight of the insoluble chloride has a positive value ranging from 0·0002+ grm. to 0·0010+ grm. with a mean of 0·0006+ grm.; and that in experiments (25), (28), (29), (30), and (31) the mean error is negative, amounting to less than 0·0001− grm., with a range from 0·0005− grm. to 0·0007+ grm.

(To be continued.)

* "Report on Researches into the Composition of Ocean Water collected by H.M.S. Challenger during the Years 1873—1876," p. 18

## ON THE ANALYSIS OF OPIUM.

By CHARLES M. STILLWELL, M.A.

In presenting a method for the analysis of opium, as an addition to the many processes published from time to time, I feel justified on account of the importance which a correct analysis of this costly substance demands. I lay claim to no special originality in the general method of the analysis to be described. Based as it is upon the processes used by Dr. Squibb for the sampling of the opium and the mode of extraction and precipitation of the morphia, I have attempted to render these still more effective by such modifications as I find necessary in the course of the analysis. The use of the two washing solutions, to be described hereafter, is an important step toward obtaining a pure precipitate of morphia; and the final purification of the crystalline precipitate, proposed by myself, I find to be absolutely necessary for the correctness of the analysis. To this latter point I call special attention. The process of Dr. Squibb, used as he directs, will give results which are almost exactly comparable among themselves. It can be used, therefore, as a control; but to obtain analytical results such as are needed for buying and selling, a still greater degree of accuracy is required. For this purpose I believe the method now to be described to be of great value. It is presented somewhat more in detail than may seem necessary, but I find in my practice that much of the value of an analytical process depends upon these small and seemingly insignificant points. For the analysis of a substance so complex in its nature as opium, it is necessary that the process used should be simple, easy of manipulation, but yet thoroughly successful in the extraction of all the morphia present. The solvent used and the bulk of the solution obtained should be such that the least possible amount of injury is done to the alkaloid during the course of the analysis.

In Allen's "Commercial Organic Analysis" is found the following account of the—

*Action of Solvents on Opium.*—The action of different solvents and reagents on opium is shortly as follows:—

"Water dissolves meconic acid readily, as also meconate and acetate of morphia; free morphia very sparingly, and narcotine still less so (1 in 1000). Narceine is more soluble than morphine, while the resin, caoutchouc, &c., are insoluble, though certain gummy matters pass into solution.

"Alcohol dissolves free morphia, as well as the acetate and meconate. The other alkaloids of opium, as also the resin and caoutchouc, are dissolved by alcohol.

"Amylic alcohol dissolves all the alkaloids of opium, if in a free state. The resin is also slightly soluble in amylic alcohol.

"Ether, benzene, and carbon disulphide dissolve about 0·05 per cent of free morphia, and the other free alkaloids of opium more readily. These solvents also dissolve the caoutchouc, but not the resin.

"Acids dissolve all the alkaloids from opium, together with the resin.

"Fixed alkalies used in excess dissolve morphine freely, while narcotine remains insoluble. Lime water dissolves morphine, but is a solvent for narcotine only in presence of morphine. The resin of opium is partly soluble in alkalies.

"Ammonia dissolves morphia sparingly, narceine and codeine readily, while the other alkaloids and the resin of opium are insoluble.

"From the foregoing statements, the arrangement of which is mostly due to Mr. E. L. Clever,* it follows that an aqueous solution of opium will contain meconate of morphine and other alkaloids, calcium salts, meconic acid, extractives, and resinous matter dissolved by the free acid present.

"An alcoholic solution will contain, in addition to the above, free narcotine, caoutchouc, fat, and resin.

"Opium which has been exhausted with water still retains a bitter taste; but this is probably due to narcotine, as it is removed by carbon disulphide, benzene, or ether, in which morphine and its salts are insoluble. If the aqueous solution be distinctly acid, water may be trusted to dissolve the whole of the morphia from opium. In some processes of assaying opium the sample is subjected to a preliminary treatment with benzene or ether to remove narcotine, caoutchouc, and colouring matter. By this means the subsequent exhaustion with water is much facilitated and a purer solution of morphine is obtained.

"In presence of much narcotine, morphine is soluble in benzene, but this is not true of the meconate or other *salts* of morphine. Hence there is no loss of morphine on extracting opium with benzene. Meconate of morphia is, however, freely soluble in a mixture of alcohol and chloroform, but the simultaneous presence of ether prevents its solution more or less completely. . .

"The ash of opium is readily determined by igniting a weighed quantity of the sample. The residue should not exceed 8 per cent.

"An aqueous solution of opium should give a red colouration with ferric chloride. The production of a

* *Year-Book of Pharmacy*, 1876, p. 502.

black or blue-black colouration or precipitate will be due to tannin, which is not a normal constituent of opium.

"Genuine opium contains no starch, and hence, on boiling with water the residue insoluble in cold water, the solution obtained should give no blue colouration with solution of iodine.

"Sand, stones, bullets, and other make-weights are sometimes met with as adulterants of opium. Sugar, gum tragacanth, pulp of apricots and figs, pounded poppy capsules, &c., are also employed for the sophistication of opium."

Of the many processes published for the estimation of morphia in opium, none have proved thoroughly successful and easy of accomplishment. In an article by Dr. E. R. Squibb, published in *Ephemeris*, Jan., 1882, is found a full account of a process used by him, and based upon one published by Prof. Flückiger some two years previous. The reader is referred to the article for the full text of the description, but the essential points are described below. The modifications of the original process introduced by Dr. Squibb, though slight, have great value, because they lead to a thorough exhaustion of the opium and a better crystallisation of the morphia.

Those analytical processes which depend on the use of lime and on the use of an aliquot portion of the filtrate are unsatisfactory, because they do not thoroughly exhaust the opium; because the discarded portion is richer in morphia than the aliquot portion taken; and, lastly, because the volume of liquid used is too large to allow of the full separation of the morphia. These points were examined by Dr. Squibb, who found in an opium of known strength that the first portion of the solution gave 0·544 grm. of morphia, the discarded portion gave 0·595 grm., and the two together did not account for the total amount of morphia present by about 1 per cent. This loss of morphia was found to be due to the large volume of solution used for the precipitation. A test made by myself on this point gave the following results:—10·18 grms. of an opium, which gave, by the process hereafter to be described, 11·76 per cent morphia, was thoroughly exhausted, and the filtered solution evaporated to 100 c.c. The requisite amounts of alcohol, ether, and ammonia were added. The precipitate obtained weighed 1·020 grms., equal to 10·00 per cent. The filtrate from the crystals was evaporated to 25 c.c. and the requisite amounts of alcohol, ether, and ammonia added, and a further precipitate of morphia weighing 0·155 grm. was obtained, equal to 1·52 per cent. The total amount found was, therefore, 11·52 per cent. In a pure salt of morphia this effect of dilution is not so important. A crystallised sulphate of morphia, which, if pure, should contain 75·2 per cent morphia, was dissolved and the morphia crystallised from a total volume of 120 c.c. of solution. The crystals obtained equalled a percent of 74·31. On evaporation of the filtrate to 25 c.c., and recrystallisation, 0·20 per cent more was obtained, giving a total of 74·51 per cent morphia.

Trails made to test the accuracy of using an aliquot portion of the solution gave results too discordant to be of any service. In one case I obtained 10·63 per cent instead of 11·76 per cent, the actual amount in the opium.

As regards the accuracy of the process about to be described, the following results may be of interest:—A lot of opium, very uneven in quality, was sampled by one of our men, and I made the analysis, obtaining—Water, 24·30; morphia, 11·75 per cent. Three months afterwards the same lot was re-sampled by myself and one of our men, and the resulting sample analysed by me, in duplicate, using different weights of opium for each analysis. The results obtained were—Water, 24·70; morphia, 11·70 and 11·82; average, 11·76 per cent. Other results of duplicate tests showing the same agreement might be given if necessary.

*Sampling.*—The process of sampling and the preparation of the sample are of great importance, as, on account of the varying quality of the lumps of commercial opium, it is very unlikely that any two lumps will be of the same strength. About every tenth lump in a case is sampled by cutting a cone-shaped piece from the middle of the lump, with an ordinary pocket-knife. From the side of this cone a small strip is taken, and the cone returned to its place in the lump. These separate strips are kept in a tin box until the sampling is finished, care being taken that they do not lose moisture by exposure.

*Preparation of the Sample for Analysis.*—The sample, composed as it is of many small pieces, is treated as follows:—A slab of glass or stone about two feet long is provided, though a small board of hard wood will answer. On this this the mass of samples is rolled with the hands, until it is worked into a long thin roll. This is doubled upon itself and rolled again, re-doubled and re-rolled, and so on until a section cut anywhere from the roll shows a perfectly homogeneous surface. The ease with which this is done depends upon the condition of the sample; a moderately dry sample—that is, with 10 to 12 per cent of water—will roll out very easily without sticking to the hands, while a wetter one will give some trouble; but with care the sample can be made perfectly uniform in so short a time that no loss of moisture will take place. The sample when prepared is wrapped in tin-foil, and placed in a suitable box or bottle to be kept for analysis.

If the sample be hard and dry, and cannot be mixed by the above method, break it up coarsely, take an average portion for moisture, and dry in the water-bath an average of the remainder, until it is possible to grind it in a mortar to a sufficiently fine powder. Determine the moisture and the morphia in the prepared sample. Then, by calculation, the result is reduced, first, to the amount present on a dry basis, and then to that present in the original sample. If the sample for analysis is powdered opium, no difficulty will occur in getting a fair average sample.

*Moisture.*—Two separate portions of the average sample, from 6 to 8 grms. each, are weighed and dried at 100° C. From samples prepared as above described, duplicates for moisture will agree very closely. For example:—

| | | | | | | |
|---|---|---|---|---|---|---|
| 1. | 24·70 | 23·13 | 22·90 | 20·30 | 17·90 | 20·60 |
| 2. | 24·70 | 23·40 | 22·70 | 20·60 | 17·50 | 20·70 |
| Average | 24·70 | 23·26 | 22·80 | 20·45 | 17·70 | 20·65 |

*Determination of the Morphia.*—Weigh off a portion of the average sample, using about 10 grms., noting the exact weight of the portion taken.

"Put the weighed portion into a flask or common wide-mouthed bottle of 120 c.c. capacity, fitted with a good cork. Add 100 c.c. of water, distilled by preference—but this is essential only when common water contains an unusual amount of inorganic matter—and shake well. Allow it to macerate over night or for twelve hours, with occasional shaking, and then shake well and transfer the magma to a filter of about 10 centims. = 4 inches diameter, which has been placed in a funnel and well wetted. As it is the shaking which accomplishes the object here in view, rather than the standing, the time of maceration can be easily shortened even to three hours, if the shaking be frequent and active."*

Instead of using a flask or bottle I place the weighed portion in a strong beaker, add 100 c.c. water, and then, with a glass rod fitted at the end with a piece of thick rubber tubbing, I rub and break up the lump of opium, until in a short time it is thoroughly disintegrated. It is best to let the opium stand some hours in order that the morphia be thoroughly extracted. In test assays it was found that if the solution were filtered off as soon as the lump of opium was broken up and no more dark, soft portions were seen, the amount of morphia obtained was less than the actual amount present. Duplicates made in this manner—by filtering as soon as the dark soluble portions were dissolved—did not agree; but by repeating the

* *Ephemeris*, i., 15.

operation and allowing the opium to digest over night, the duplicates, made with different amounts of opium, agreed exactly in the amount of morphia obtained. The beaker is covered with a watch-glass and placed where no ammoniacal vapours will affect it, although, as the water solution is acid from the organic acids present in the opium, no precipitation of morphia will take place until this acidity be neutralised.

I learn from Dr. Squibb that he has lately adopted the plan of adding a few drops of sulphuric acid to the water used for the exhaustion of the opium. The solution is kept slightly acid, and the extraction of the morphia seems to be thereby facilitated.

"As rare exceptions, some powdered opiums will be found which, through natural conditions, give a magma with water which will not filter, or filter so very slowly that the water solvent becomes impracticable. When this is discovered the magma is thrown away and a fresh portion of powder is taken. Wash this by agitation in a bottle with 30 c.c. of ether (sp. gr. 0·728), transfer it to a filter, rinse the bottle with 20 c.c. more of ether, and pour this on to the opium in the filter. When this has passed through, wash the filter and opium with 10 c.c. more ether, applied drop by drop around the edges of the filter and on the surface of the opium. Then dry the powder on the filter and use it as in the case of opium, which does not need to be first washed with ether.

"Opium which is adulterated, or standardised by admixture with dextrine, gums, sugar, or glucosides, yields an impracticable magma with water, and ether-washing to such does little or no good. All such samples have to be exhausted with an alcoholic solvent. If not much adulterated a mixture of equal measures of alcohol (sp. gr. 0·820) and water will answer best, but generally a mixture of two measures of alcohol (sp. gr. 0·820) with one measure of water is to be used, instead of water alone, for the exhaustion, and as this mixture is not as good a solvent for the morphia salts in the opium as water, more of it is required, and the washing and percolating should be carried to 250 c.c. of solution from the 10 grms. of opium. The process after exhaustion is the same as where water is used as the solvent."*

(To be continued.)

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, January 20th, 1887.*

Dr. Hugo Müller, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Leonard Dobbin, Ph.D., 4, Cobden Road, Edinburgh; Edgar Hall, Town House, Queenboro', Kent; Alexander Hay, 84, West Parade, Lincoln; John Steele Jackson, The College, Epsom; George McGowan, Bangor, North Wales; Henry Droop Richmond, Park Lane, Tottenham; Arthur H. F. Kuppel, 52, Parrock Street, Gravesend; Henry Lloyd Snape, B.Sc., The Technical School, Manchester; W. Scrutton, University College, London; Arthur Stanley, 38, Trebovir Road, Earl's Court, S.W.; Henry Weston Wallis, 7, Auckland Road, Clapham Junction, S.W.

The following papers were read:—

1. "*Some Silicon Compounds and their Derivatives.* By J. Emerson Reynolds, M.D., F.R.S.

Although large numbers of silicon analogues of carbon compounds are known, it is pointed out that we do not find among the former any well-defined representatives of cyanogen and its derivatives. The present investigation was commenced some years ago with the primary purpose of obtaining such compounds, if possible, and generally of examining reactions in which the silicon haloids—particularly the tetrabromide—and organic nitrogen compounds take part. In the course of the work a number of new bodies have been obtained, only a few of which can, however, be regarded as cyanogen derivatives.

The author, in this the first paper of a series, describes the action of silicon tetrabromide on thiocarbamide, as the products obtained in this branch of the enquiry were exhibited at the *conversazione* of the Royal Society last June.

It is shown that silicon tetrabromide in benzene solution acts in a very remarkable manner with thiocarbamide. the latter affording a condensed amide with which the tetrabromide unites. Eight molecules of thiocarbamide combine with only one of silicon tetrabromide at the temperature of boiling benzene. Attempts to make this amide unite with a larger proportion of the bromide only lead to decomposition. The product is a thick liquid at a temperature 65° C., below the fusing-point of pure thiocarbamide (140° C.), and becomes solid at ordinary temperatures. Solvents of the tetrabromide do not extract any from this product, nor is it dissolved by any liquid without decomposition.

When boiled with anhydrous alcohol it affords a monobromo-derivative of pentathiocarbamide, which is obtained from the alcoholic solution in beautiful groups of silky crystals. At the same time bromethyl-thiocarbamide and bromethyl-dithiocarbamide are obtained along with ethylic silicates.

Discussion.

In reply to Mr. Rideal, Prof. Reynolds said that in preparing silicon tetrabromide it was essential to use silica which had been precipitated in the gelatinous form, and to mix it most intimately with the carbon (lamp-black); the action of the bromine took place at an extremely high temperature. Replying to the President's question, Had analogous compounds been obtained from urea? he said that urea did react with silicon tetrabromide, but not in the same way as thiocarbamide.

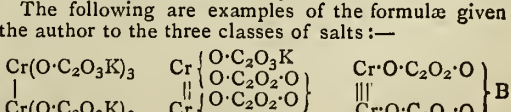
Dr. Armstrong remarked that, assuming the bromine to be the linking agent, it was noteworthy that in the silicon compound, and also in that of ethyl bromide with thiocarbamide, the ratio was Br : $2CSN_2H_4$: this perhaps might be regarded as an indication that the thiocarbamide molecule had at least the formula $C_2S_2N_4H_8$; the ratio in the remarkable compound with bromine was, however, different.

2. "*Chromo-organic Acids.* Part I. *Certain Chromoxalates.*" By Emil A. Werner.

This paper contains an account of the salts resulting from the combination of chromium oxalate with certain metallic oxalates. A study of these compounds has led to the conclusion that they cannot be considered as ordinary double salts, but are in point of fact salts of complex chromoxalic acids. A similar view of the constitution of these compounds was advanced by Malaguti in 1843, but strange to say has been entirely ignored, since all workers with these particular compounds (with the exception of Clarke and Kebler) have treated them as double or triple salts. Malaguti's view has been considerably extended, and new experimental evidence furnished in support of it; it has also been shown that the oxalic radicle can be displaced by those of other organic acids, salts of which have been obtained.

The paper concludes with the description of a new series of chromoxalates, whose members are shown to be closely related to those already known.

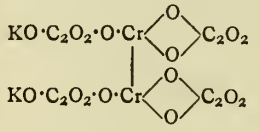
The following are examples of the formulæ given by the author to the three classes of salts:—




* *Ephemeris*, i., 15.

Discussion.

Dr. Japp thought that some of the provisional constitutional formulæ proposed by the author for the various series of chromoxalates were open to criticism. In the formula for the salt of the "red series," for example, two oxygen-atoms, united to oxalic acid radicles, were represented as satisfying each other's affinities—an arrangement which would place these stable salts in the same category as the explosive peroxides of acetyl and benzoyl, whilst at the same time the two chromium-atoms in the formula were doubly linked. It was only necessary, however, to suppose that these vacant affinities of the chromium-atoms were satisfied by those of the oxygen-atoms in order to represent the salts as perfectly normal, thus :—



The constitution of the salts of the "green series" was still more anomalous, as in these the chromium was represented as existing in a less saturated state than that in which it occurs in the chromous compounds.

Mr. J. M. Thomson drew attention to the interesting dichroic properties of the chromoxalates, the dichroism being especially marked in the case of the calcium salt described by Prof. Hartley. The difference in the extent to which they exhibit dichroism was very remarkable, as it distinctly decreased as the atomic weight of the metal forming the double chromoxalate increased, the dichroism of the potassio-baric chromoxalate being small compared with that of the potassio-calcic chromoxalate or the potassio-lithic chromoxalate. Had the author observed the same diminution of dichroism with increase in molecular weight in the salts formed from the organic bases which were mentioned in the paper? With the object of further examining the optical properties of these compounds, the speaker had recently prepared double potassio-chromoxalates containing nickel and cobalt; these salts, however, presented no specially marked dichroic properties. They are also more soluble than the calcium or barium salts, and more difficult to crystallise.

Dr. Forster Morley said that the "red salt," as formulated would be a chrom*ous* salt; spectrum analysis might be expected to throw light on the question whether it actually was a compound of this order. From observations recently made in the laboratory of the University College, it appeared that the difference between the blue and red chromoxalates was of the same nature as between the known blue and red chrom*ic* salts.

Dr. Armstrong, agreeing with the previous speaker, said that a chrom*ous* salt, such as the red salt was represented to be, ought, like all chromous salts, to be a powerful reducing agent: not a word was said in the paper to indicate that such was the case. The green salt, according to the formula given, would be still more oxidisable: it was inconceivable that such a salt should be formed in presence of alkali and air. He thought all three were chrom*ic* salts.

Prof. Reynolds, by whom the paper was read, said, in reply, that differences in dichroic properties, such as were referred to by Mr. Thomson, had been noticed in the case of the salts of organic radicles. The author was studying the spectroscopic behaviour of the salts described.

3. "*Note on the Constitution of the Double Chromic Oxalates.*" By W. N. Hartley, F.R.S.

Some years ago (*Proc. Roy. Soc.*, xxi., 499) the author described a remarkable dichroic salt, a potassio-calcium chromoxalate, and at the same time he prepared a large number of similar salts, the analyses of which were not completed in time for publication. These were potassio-chrome oxalates containing strontium, barium, lithium, and thallium. Excepting the lithium salts they did not possess any striking optical properties. They crystallised freely.

On account of the manner in which these salts were formed, for instance :—

*a*. By dissolving chromic hydrate in oxalic acid, and adding the bases or their carbonates;

*b*. By preparing the red potassium chromic oxalate, $Cr'''KC_4O_8{\cdot}3H_2O$, and adding neutral potassium oxalate thereto;

Also by reason of their reactions with calcium, strontium, and barium salts, he came to the conclusion that they were really derivatives of a distinct acid which might be termed chromoxalic acid, and the formula following would represent its constitution—$Cr'''O_3(C_2O{\cdot}OH)_3$.

The following reasons may be stated as affording grounds for this view :—

1. The chromium is not precipitated by alkalies.

2. When alkali is added a soluble salt of the alkali is produced instead of a precipitate of chromic oxide or hydrate.

3. The carbonates of the alkalies give soluble salts of the alkalies and no precipitate.

4. The formula given is the only one which explains the formation of such salts as $K_3Cr'''{\cdot}3C_2O_4$.

5. The blue salts such as $K_3Cr'''{\cdot}3C_2O_4$ are *formed with greater facility* than the red salt $KCr'''{\cdot}2C_2O_4$.

6. The blue salts give none of the reactions which are characteristic of oxalates, such as precipitation with chlorides of calcium, barium, &c.

7. The blue salts can be formed from the red, and the potassio-calcium chromic oxalate can be made by boiling calcium oxalate with the red salt according to the equation—

$$\left.\begin{matrix}K\\Cr'''\end{matrix}\right\}2(C_2O_4) + Ca''C_2O_4 = \left.\begin{matrix}KCa''\\Cr'''\end{matrix}\right\}3(C_2O_4).$$

4. "*Remarks on Recent Papers by A. Baeyer and J. Thomsen on 'The Constitution of Benzene.'*" By Alex. K. Miller, Ph.D.

The author contends that most of Baeyer's arguments fail to carry much weight, since they are based on reactions which admittedly involve intramolecular changes. Such reactions might be used with equal force either in support of or against almost any formula, according to the way in which the isomeric change be assumed to take place. It is shown, for instance, how the conversion of dihydroxyterephthalic ether into succinosuccinic ether may be explained with the help of the prism formula as readily as with Kekulé's symbol. The author also points out a weak point in the argument which Baeyer brings forward against the prism formula. Finally it is pointed out that Baeyer's arguments in support of the existence of a double bond in benzene are founded upon data which may perhaps be used as an argument in favour, but certainly do not prove the existence, of a pair of double bonds.

With reference to Thomsen's octahedral symbol for benzene, it is stated that the advantages claimed for it, namely, that it is a perfectly symmetrical space representation which admits of three possible disubstitution-derivatives, and three only, are perfectly well founded. It is, however, pointed out that the symbol differs in some important respects from Kekulé's symbol; it is impossible, for instance, to represent quinone as a diketone, the only representation possible being that in which each oxygen-atom is united by one affinity only to a carbon-atom; another difference is that Thomsen's symbol renders possible *four* disubstitution-derivatives of hexahydrobenzene. Finally, certain synthetical reactions, such as the formation of succinosuccinic ether from succinic ether, cannot well be represented with the aid of the symbol in question.

In conclusion, the author expresses the opinion that neither Baeyer's nor Thomsen's paper has contributed to the solution of the problem of the constitution of benzene.

At the next meeting, on February 3rd, there will be a ballot for the election of Fellows, and the following papers will be read:—

"An Explanation of the Laws which govern Substitution in the case of Benzenoid Compounds," by Dr. Armstrong. "The Synthetical Formation of Closed Carbon Chains. Part II. Some Derivatives of Tetramethylene," by Dr. W. H. Perkin, jun., and H. Coleman. "Part III. Some Derivatives of Pentamethylene," by Dr. W. H. Perkin, jun.

## PHYSICAL SOCIETY.

*January 22nd*, 1887.

Prof. H. McLeod, F.R.S., Vice-President, in the Chair.

Dr. F. Wormach was elected a member of the Society.

The following papers were then read:—

"*The Permanent and Temporary Effects on some of the Physical Properties of Iron, produced by raising the Temperature to* 100° *C.*" By Mr. Herbert Tomlinson, B.A.

The paper is divided into three sections: 1st, Internal Friction of Iron; 2nd, The Longitudinal and Torsional Elasticities of Iron; and 3rd, The Velocity of Sound in Iron.

In his experiments on the internal friction of metals, the author uses a vertically suspended wire, rigidly clamped at its upper extremity, and having its lower end secured to a horizontal bar of metal, attached to which are two cylinders of equal mass and dimensions, placed at equal distances from the wire. When the system is set in torsional oscillation the amplitude gradually diminishes, due to the internal friction of the metal and the friction of the air. The combined effect is measured by the logarithmic decrement of the oscillations, and the air effect eliminated by Prof. Stokes's formulæ and the author's experimental determination of the viscosity of air. When the deformations are sufficiently small the experiments prove that the logarithmic decrement of air is independent of the amplitude and period of vibration. These results are only true when the wire has been allowed to rest a considerable time after any change has been made in the arrangement, and when there have been a large number of oscillations executed previous to the actual testing.

Reference is made to some experiments by Prof. G. Wiedemann, which show that when a wire is subjected to torsional stress it does not recover itself when the stress is gradually reduced to zero, but remains permanently twisted through a small angle (say $\theta$). By reversing the twisting couple there is a permanent set on the other side of the initial position. If the operations be repeated, $\theta$ diminishes and attains a minimum. The period during which this diminution takes place is called the "accommodation period."

When a wire is in torsional vibration the position of equilibrium is continually shifting to and fro, through twice the above minimum angle, and Wiedemann considers the loss of energy to be due to this shifting. The author's experiments verify Wiedemann's results, and also show that time and temperature have great effect on the internal friction. By repeatedly heating to 100° C. and slowly cooling an annealed iron wire for six days, the logarithmic decrement due to internal friction was reduced to about one-eighth its original amount, at the same temperature, and when the wire was maintained at 98° C. the decrement was reduced to 1-30th.

The author considers the permanent diminution produced by heating and cooling to be mainly due to the slow shifting backwards and forwards of the molecules, induced by that process.

In the second part of the paper it is shown that the effects of change of temperature on the longitudinal and torsional elasticities of iron and steel are not nearly so great as that produced on the internal friction. Thus, by heating annealed iron wire its longitudinal and torsional elasticities are slightly decreased, but on cooling there is a permanent increase in both. Time is also an important element, for a long rest after cooling still *further* increases both elasticities. From the above results it is evident that the velocity of sound in iron and steel must *diminish* with rise of temperature. This was experimentally proved before the meeting. Attention was particularly directed to this fact because most of the best text-books make the opposite and erroneous statement.

Remarks were made by Mr. C. V. Boys, and the Chairman mentioned a new form of clock whose action depends on torsional elasticity of a steel wire.

"*On some New Measuring Instruments used in Testing Materials.*" By Prof. W. C. Unwin, F.R.S.

In most measuring instruments previously used it has been considered sufficient to make the measurement of elongation from one side of the bar, but this, the Professor showed, was liable to serious errors owing to the fact that test bars are not always perfectly straight, and to the possibility of originally straight bars being bent by improper fixing in the testing machine. In such cases the modulus of elasticity calculated from the apparent elongations are subject to considerable error. In endeavouring to overcome these difficulties the author has devised several new forms of measuring apparatus, which are attached to two sides of the bar by steel points, and the mean elongation of the two sides determined.

The first apparatus described consists essentially of sliding callipers read by a microscope to 1-10,000th of an inch. Another form has two clamps provided with sensitive levels. Each is attached to the bar by two steel points, the line joining which is perpendicular to the direction of the stress, and the clamp can rotate in a vertical plane about this line as an axis. The lower clamp is levelled by a screw pressing against the surface of the bar, and the upper one by means of a micrometer screw parallel to the axis of the bar, the nut of which is secured to the bottom clamp. By this means the elongation can be measured to 1-10,000th of an inch. In a third form two similar clamps without levels are kept apart by a steel rod ending in knife edges. One of the clamps carries a small roller, which turns about an axis parallel to the line joining the steel points above mentioned, and the axis carries a small plane mirror. The other clamp supports a projecting arm parallel with the axis of the test piece, and which presses on the surface of the roller. When the bar is elongated the mirror is turned through a small angle, and the elongation is determined by a reading telescope and vertical scale, to 1-100,000th of an inch. A similar apparatus is used for testing the compression of stone, but in this the compression is multiplied by a lever and measured by a micrometer microscope to 1-100,000th of an inch.

Mr. C. V. Boys directed attention to some beautiful photographs of the solar spectrum just received from the Johns Hopkins University, which had been obtained by Prof. Rowland's concave gratings.

At the conclusion of the meeting Prof. Unwin invited the members to visit the Engineering Laboratory of the City and Guilds of London Central Institution, where he broke a bar of Staffordshire iron in the 100 ton testing machine, the force and elongation being automatically recorded.

**Absorption Spectrum of Oxygen.**—Prof. Olszewski laid before the Vienna Academy of Sciences determinations of the boiling-point of pure ozone (−106°), and the congealing-point of ethylene (−169°), whereby he used liquid oxygen as a refrigerant. He has determined the absorption spectrum of the latter, and observed two conspicuous bands. One band is in the red, to the right of Frauenhofer's C line, and the second in the yellow, to the right of D. Both agree with the telluric absorption-bands of the solar spectrum, corresponding to the wave-lengths 629 $\mu$ and 577 $\mu$ both in position and appearance.—*Chem. Zeitung*.

## NOTICES OF BOOKS.

*The Toxicity of Silicon Fluoride.* By Sir Charles A. Cameron, M.D., Ex-President and Professor of Chemistry and Hygiene, R.C.S.I.

This pamphlet is a reprint from the *Dublin Journal of Medicine* for January, 1887, and it is of interest to the manufacturer of artificial manures, to sanitarians, and to physiologists.

The author accounts for the death of two men who worked in an artificial manure works, on the assumption that they inhaled silicon fluoride, a gas evolved in making superphosphate of lime. He shows that the phosphate used in the works contained 6·36 per cent of calcium fluoride, and that a ton of it, if treated with a full complement of sulphuric acid, would evolve 32·78 cubic metres of silicon fluoride gas. He gives elaborate accounts of his examination of the lungs, heart, &c., of the last man killed, as he believes by inhaling silicon fluoride, and, from this examination and from the symptoms during illness concludes that fluoride of silicon caused his death. In the lungs traces of fluorine and 0·75 grm. of silica were found.

Experiments made with rats and guinea-pigs proved that silicon fluoride was more poisonous than carbonic oxide; 0·5 per cent rendered air rapidly fatal to a guinea-pig.

The author shows that silicon fluoride is more complex in its physiological action than carbonic acid. It causes partial asphyxia by depositing colloid silica in the bronchi and in the air vesicles of the lungs, which is not absorbable into the circulation. Unlike $CO_2$ it does not appear to affect the psychical nerve-cells, as the two men poisoned by the gas were conscious to the last. The fluosilicic acid which the silicon fluoride forms on coming into contact with the moist respiratory passages is taken up into the circulation, and it apparently acts directly upon the filaments of the pneumogastric nerve which come directly in contact with it, and it probably also acts on the inhibitory ganglionic centres in the walls of the heart, already embarrassed by the impure condition of its blood due to deficient aëration: in this case the immediate cause of death would be failure of the heart's action, the patient retaining consciousness to the last.

The author believes that the fluosilicic acid acts as a poison to the nerve-centres controlling respiration, and believes that the solid fluosilicic acid acts as a mechanical stimulus to the nerves of the smaller bronchi, causing their muscles to contract spasmodically, and thereby diminishing the area of the passages from the trachea to the air-vesicles of the lungs.

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*The Retrospect of Medicine.* Being a Half-yearly Journal, containing a Retrospective View of every Discovery and Practical Improvement in the Medical Sciences. Edited by James Braithwaite, M.D. (London). Vol. xciv. July—December, 1886. London: Simpkin, Marshall, and Co.

This useful repertory contains nothing novel concerning the action, the detection, or the extirpation of deadly microbia. Nor do we find any discussion on Pasteur's treatment of hydrophobia.

Dr. F. Cresswell recommends a modification of Fehling's solution for detecting and estimating sugar in urine. He takes 35 grms. of copper sulphate, dissolves it in 200 c.c. of glycerin, and 100 c.c. of water, adds 80 grms. sodium hydrate previously dissolved in 400 c.c. of water, and boils the mixture for fifteen minutes. The liquid is made up to 1 litre with distilled water, and is then let stand until clear. This mixture is preferable to Fehling's solution, as it is very much more permanent, and is scarcely attacked by uric acid.

Dr. G. Johnson uses, instead of Esbach's reagent for albumen in urine, a solution of picric acid, 5 grains to the ounce.

Dr. G. H. Savage calls attention to the increasing abuse of chloral, a vice now spreading alike among over-worked professional men and among fashionable idlers. We may ask what is gained by the temperance movement if ether, chloral, coca, and opium are substituted for wines and malt liquors?

In a paragraph by Dr. Schröder, on the action of various anthelmintic drugs upon *Ascaris lumbricoides*, we felt somewhat shocked at seeing this creature referred to as "the insect."

## CORRESPONDENCE.

### CHROMIC ACID COMBUSTION.

*To the Editor of the Chemical News.*

Sir,—If Dr. Burghardt will read our first communication on this subject (Chemical News, vol. lii., p. 207), referred to in the second note upon which he has based his letter of criticism, he will find he has made two serious mistakes:—

*First*, as to the method in question. What we have proposed is an anhydrous combustion, the substance being burned by $CrO_3$ in contact with $H_2SO_4$, and the estimation of the evolved gases—in many cases a mixture of CO and $CO_2$—by measurement of volume. Dr. Burghardt's method (Chemical News, vol. liii., p. 271) appears to be an aqueous combustion, with a gravimetric estimation of the carbonic anhydride, assumed to be, as in this case it may be, the only gaseous product.

*Second*, as to priority of date of publication. We need only point out that there is a difference of some months in favour of the first named.

Regretting the necessity of trespassing on your space,—We are, &c.,

E. F. Cross and E. J. Bevan.

Laboratory, 4, New Court, Lincoln's Inn, London,
January 22, 1887.

### ON THE COMPOSITION OF HYDRATED SALTS.

*To the Editor of the Chemical News.*

Sir,—In answer to M. Maumené's enquiries (Chemical News, vol. liv., p. 33) I beg to state—

1st. That the term "ordinary," as applied by us to alum, was certainly not intended to mean "impure." The alum which I examined was re-crystallised several times, and some specimens were prepared from pure alumina and pure potash, and others from metallic aluminium.

2nd. My statement was that pure alum crystallised in the ordinary way, and not subjected to the action of any desiccating agents, contains exactly 24 $H_2O$, and no more. As my work on the subject was performed in 1881 I may be excused for not apologising to M. Maumené for omitting at the time to consult his note of 1886. (With reference to desiccated alum, see *Chem. Soc. Trans.*, 1886, 12.)

3rd. I most unhesitatingly deny that pure crystallised magnesium sulphate contains 6·67 $H_2O$ only. It contains exactly $7H_2O$.

4th I have never examined calcium chloride carefully.

5th. I do not for one minute call in question the even Arcadian simplicity of "equal weights" as the basis of chemical combination, but that it is capable of explaining the composition of all compounds *without any exception*, or, as far as I know, of any compounds at all, I utterly deny.—I am, &c.,

Spencer Pickering.

## NATIVE ALLOY OF IRON AND NICKEL.

*To the Editor of the Chemical News.*

Sir,—Noticing under the heading of "Miscellaneous" (Chemical News, vol. liv., p. 310) a paragraph upon "Native Alloy of Nickel and Iron," being an announcement by the President of the Geological Society on December 1st, and communicated by Prof. Ulrich, of Dunedin, N.Z., stating that the sands of certain rivers flowing from Olivine Enstatite rocks, in the interior of South Island of New Zealand, contain metallic particles which proved to be an alloy of nickel and iron, please allow me to say that most rivers which run through districts abounding with eruptive rocks deposit sands containing metallic iron, as nearly all eruptive rocks contain metallic iron, and there are very few deposits of serpentine but what contain both metallic iron and nickel. Many of the gabros contain a similar compound of pure iron and nickel as that spoken of by Prof. Ulrich. I have tried the basalt of Ireland, Scotland, and Rouley Regis; hornblendes from Cornwall, Germany, Scotland, Norway, and America; and granite from many places,—and all contain metallic iron. Serpentine from the Lizard, Cornwall, Island of Lewis, Canada, Scotland, Germany, and Norway, and the Ural, I have found to contain the compound of metallic nickel and iron, together with oxide of nickel, sometimes as much as 0·6 to 0·7 per cent. I have found many of the Norwegian Swedish gabros contain metallic nickel combined with iron, not as sulphides, but as magnetic particles of malleable iron and nickel.

As regards the prevalence of native iron in eruptive rocks, anyone may convince himself of this by grinding a portion down in an earthenware mortar, and carefully washing (say) 100 grains of material down to about 10 grains, and then completing the levigation in an agate mortar by grinding very fine and carefully washing: the last few particles that remain in the mortar will be found to be metallic iron, or an alloy of iron and nickel when from serpentine, or from gabros when from nickeliferous district.—I am, &c.,

A. Merry.

Bryn, Heulog, Swansea, January 20, 1887.

## ANALYSIS OF HOOFS AND HORNS.

*To the Editor of the Chemical News.*

Sir,—In reference to the "Note on the Analysis of Hoofs and Horns" (Chemical News, vol. liv., p. 314) I should think Kjeldahl's method would be found far superior to the soda-lime method for determining nitrogen in hoofs, horns, shoddy, and such like nitrogenous substances.

By the use of Kjeldahl's method all the nitrogen would be recovered as ammonia, and consequently errors such as that described in the last paragraph of the note referred to would be avoided.—I am, &c.,

D. A. L.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Bulletin de la Société Chimique de Paris.*
Vol. xlvi., No. 12, December 20, 1886.

**Pyrometric Measurements at High Temperatures.**—MM. Ch. Lauth and G. Vogt.—After criticising the existing pyrometers, including the circulating water-pyrometer devised by one of them, they propose to place in different parts of the furnace in question substances capable of melting and to observe the moment at which they enter into fusion. If the melting-points of these substances are known, we have precise information as to the temperature reached at this moment. These indicators, which the authors call "fusible watches," were made at first of alloys of silver and gold for temperatures below 1075°, and of gold and platinum for greater heats. Alloys of silver and gold give exact and constant results, but those of gold and platinum are trustworthy only if they contain proportions of platinum not exceeding 15 per cent (melting-point 1160°). If the proportion of platinum is greater, a portion of the alloy rich in gold melts out first, whilst the remainder, richer in platinum, only melts at a higher temperature, thus rendering the indications doubtful. This circumstance, joined to the costliness of the alloys, led the authors to form their "fusible watches" of different materials. They form No. 1 watch of a mixture of pegmatite 51 per cent, sand 14, chalk 20, melted borax 15. They make a mixture of pegmatite 70 and chalk 30 per cent, and from this they make up their remaining "watches" as follows:—No. 2 is formed of No. 1 15 parts and 85 of the above mixture; No. 3, mixture 80 and hydrated silicate of alumina 20; No. 4, mixture 60 and hydrated aluminium silicate 40.

**The Combination-Heats of the Monobasic or Homologous Acids.**—MM. H. Gal and E. Werner.—Already noticed.

**Determination of the Neutralisation-Heats of the Malonic, Tartronic, and Malic Acids. Remarks on the Neutralisation-Heats of the Homologues of Oxalic Acid and of the corresponding Hydroxylic Acids.**—MM. H. Gal and E. Werner.—Already noticed.

**Composition of the Alkaline Permanganates.**—F. M. Raoult.—It results that the true formula of permanganic acid is $HMnO_4$, so that the molecule of this acid contains really an odd number of atomicities.

**A Rapid Method of Separating Gold and Platinum from Antimony, Arsenic, and Tin.**—Ph. J. Dirvell.—Inserted in full.

**Water of Combination of the Alums.**—M. Maumené.—Already noticed.

**Chlaurose-Phosphorous Ethers.**—L. Lindet.—The ethylic and methylic ethers have both analogous chemical properties. The former is scarcely attacked by light; the methylic ether is more so, and is slightly blackened in the course of a few days, with reduction of gold. Both are stable as regards heat, the ethylic ether being able to bear the temperature of the water-bath for some time. Above 100° it is decomposed. Both are soluble in alcohol, ether, benzene, and are recovered unchanged on the evaporation of the solvent. Both are insoluble in water, which does not exert any marked reductive action upon them.

**Successive Separation of Copper, Cadmium, Zinc, and of Nickel or Cobalt, Iron, and Manganese.**—M. Carnot.—Already inserted.

*Journal de Pharmacie et de Chemie.*
Fifth Series, Vol. xiv., No. 10, November 15, 1886.

**Is Linseed Meal a Medicine?**—P. Carles.—From this purely pharmaceutical paper we merely extract the remark that the flesh of animals, and especially of poultry, fed upon linseed cake is indigestible, and of a bad flavour.

**Coloured Reaction produced by Sulphuric Acid and Morphine.**—MM. Gasselin and Lévy.—A note recently reproduced by the *Journal de Pharmacie* indicates, as characteristic reactions of morphine, the colourations given by the successive action of sulphuric acid in presence of potassium arseniate, of water, and of ether or chloroform. M. Jorissen, of Liège, indicated, in 1879, an analogous colouration, produced under the influence of sulphuric acid alone, of water, and of ether or chloroform. The authors, on repeating the experiment, find that the colouration is produced as distinctly with pure sulphuric

acid as with the same acid mixed with an arseniate. Pure codeine produces the same colouration with less intensity.

**Auropotassic Reagent for the Detection of Glucose.**—C. Agostini.—Already noticed.

No. 11, December 1, 1886.

**Report Presented on Behalf of the Chemical Section, on the Researches of M. Moissan on the Isolation of Fluorine.**—M. Debray.—The substance of this report has been already given.

**Remarks on the Detection and the Colorimetric Determination of Salicylic Acid.**—M. Frehse.—The general process is that founded upon the reaction of ferric chloride, but certain precautions are necessary to obtain good results. The standard liquid with which the check determination is made should be recent. A second condition is always to extract the salicylic acid (contained in mixtures) by means of ether, and not to attempt its direct determination in slightly coloured liquids. The solution of ferric chloride employed must be very dilute, as a slight excess destroys the colouration. In distillation a part of the salicylic acid is carried away with the watery vapour.

**Saturation of Normal Arsenic Acid by Lime-, Strontia-, and Baryta-Water.**—Ch. Blarez.—Already noticed.

**Separation and Determination of Albumenoid Matter in Kystic Ovarian Matters, and in Ascitic Liquids.**—G. Dumonthiers.—For this paper, which is chiefly of a medical interest, we must refer to the original.

No. 12, December 15, 1886.

**New Reaction of Tannin.** — J. W. Moll. — As reagents for micro-chemical research the author recommends a saturated solution of copper acetate in which sections of vegetable tissues, &c., are steeped for seven to ten days. They are then transferred for a few minutes to a dilute solution of iron acetate. The sections are then washed in water.

**Novel Reactions of Sugar.**—H. Molisch.

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**New Scientific Journal.**—We have received the prospectus of a new scientific journal, the *Zeitschrift für Physicalische Chemie*, which will be edited by Professor W. Ostwald, of the Riga Polytechnicum. It will be devoted to physical chemistry, stœchiometry, the doctrine of affinity, &c. Among the contributors we notice the names of Lothar Meyer, D. Mendeleeff, N. Menschutkin, Nilson and Pettersson, of Stockholm, and Thomsen, of Kopenhagen.

## MEETINGS FOR THE WEEK.

MONDAY, 31st.—London Institution, 5.
—— Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "The Diseases of Plants," by Dr. Thudichum.
TUESDAY, Feb. 1st.—Institution of Civil Engineers, 8.
—— Royal Institution, 3. "Function of Respiration," by Prof. Arthur Gamgee, F.R.S.
—— Society of Arts, 8. "The Condition of Applied Art in England, and the Education of the Art Workman," by T. Armstrong.
—— Pathological, 8.30.
WEDNESDAY, 2nd.—Society of Arts, 8. "Sewage Irrigation," by Alfred Carpenter, M.D.
THURSDAY, 3rd.—Royal, 4.30.
—— Chemical, 8. Ballot for the Election of Fellows.
—— London Institution, 6.
—— Royal Institution, 3. "Molecular Forces," by Prof. A. W. Rücker, F.R.S.
—— Royal Society Club, 6.30.
FRIDAY, 4th.—Geologists' Association 8.
—— Royal Institution, 9. "Some Unpublished Records of the City of London," by Edwin Freshfield, LL.D.
SATURDAY 3th.—Royal Institution, 3. "Modern Composers of Classical Song—Johannes Brahms," by Carl Armbruster.

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THE CHEMICAL NEWS.

Vol. LV. No. 1419.

## FERRIC CHLORIDE AS AN EXCITING AGENT FOR VOLTAIC BATTERIES.

By H. N. WARREN, R.A.

Based upon the reducing action that zinc exerts over an acidified solution of potassium bichromate is the construction of the well-known bichromate battery; and on a somewhat similar theory of reduction I have lately found an acidified solution of ferric chloride mixed with bromine to answer the purpose still more energetically, and at the same time assuming a constant action, a point which has long been desired with respect to the bichromate battery, the construction of the battery itself being almost identical with the bichromate-bottle form, but charged with a concentrated solution of ferric chloride with a layer of bromine at the bottom, the solution being slightly acidified. Thus ferric chloride being far more soluble in water than potassium bichromate in the first instance, a much stronger solution may be obtained; the bromine so acting as to continuously convert the ferrous chloride, formed by the reduction of the zinc, back to ferric chloride; and in thus doing maintaining a constant action. With respect to the power of the electrical current produced I have found it to be the most powerful yet examined, two small half-pint cells decomposing water most energetically, and three similar cells, heated to intense whiteness two inches of fine platinum wire; whilst four large size cells, charged with the same solution, gave an intense arc between two graphite points, and very perceptibly volatilised platinum; all the more oxidisable metals, as well as silver and gold, were dissipated with great brilliancy when introduced between the points; the strength of the battery is slightly impaired after three hours' action, owing to the reducing action of the zinc somewhat overcoming the oxidising effects of the bromine, but on allowing the battery to stand a short time, it fully recovers its original power. The bromine being once consumed may be again liberated by the introduction of a small quantity of bleaching-powder, thus rendering the battery in every respect more constant, more powerful, and at the same time less costly in its construction than any other form of voltaic battery.

## EXAMINATION OF BUTTER COLOURS.

By H. B. CORNWALL.

Several of our States have forbidden the addition of colouring-matter to butter substitutes in imitation of the yellow colour of genuine butter, so that our chemists frequently have to make tests for such added colours.

Not one of the published methods tried by the writer gave much satisfaction; some failed to extract colouring-matters known to have been added, others gave emulsions which were entirely useless for examination, and the writer consequently tried to find some better method.

The following gave perfect satisfaction so far as regarded the separation of annatto, which is the chief ingredient of every commercial butter colour met with by the writer:—

About 5 grms. of the warm filtered fat are dissolved in about 50 c.c. of ordinary ether, in a wide tube, and the solution is vigorously shaken for ten to fifteen seconds, with 12 to 15 c.c. of a very dilute solution of caustic potash or soda in water, only alkaline enough to give a distinct reaction with turmeric paper, and to remain alkaline after separating from the ethereal fat solution. The corked tube is set aside, and in a few hours, at most, the greater part of the aqueous solution, now coloured more or less yellow by the annatto, can be drawn from beneath the ether with a pipette, or by a stopcock below, in a sufficiently clear state to be evaporated to dryness and tested in the usual way with a drop of concentrated sulphuric acid.

Sometimes it is well to further purify the aqueous solution by shaking it with some fresh ether before evaporating it, and any fat globules that may float on its surface during evaporation should be removed by touching them with a slip of filter-paper; but the solution should not be filtered, because the filter-paper may retain much of the colouring-matter.

The dry, yellow, or slightly orange residue turns blue or violet-blue with sulphuric acid, then quickly green, and finally brownish or somewhat violet (this final change being variable, according to the purity of the extract).

Saffron can be extracted in the same way; it differs from annatto very decidedly, the most important difference being in the absence of the green colouration.

Genuine butter, free from foreign colouring-matter, imparts at most a very pale yellow colour to the alkaline solution; but it is important to note that a mere green colouration of the dry residue on addition of sulphuric acid is not a certain indication of annatto (as some books state), because the writer has thus obtained from genuine butter, free from foreign colouring-matter, a dirty green colouration, but not preceded by any blue or violet-blue tint.

Blank tests should be made with the ether; but it is easy to obtain ether that leaves nothing to be desired as to purity.

Turmeric is easily identified by the brownish to reddish stratum that forms between the ethereal fat solution and the alkaline solution before they are intimately mixed. It may be even better recognised by carefully bringing a feebly alkaline solution of ammonia in alcohol beneath the ethereal fat solution, with a pipette, and gently agitating the two, so as to mix them partially.

John C. Green School of Science,
Princeton, New Jersey.

## EXAMINATION OF A SPECIMEN OF QUARTZITE.

By PHILIP HOLLAND,
Public Analyst for Southport.

I am indebted to Mr. Parson Smith, of Shrewsbury, for the sample. The stone is quarried at Nill's Hill, Pontesbury, and is sold as paving setts and for road-mending. My sample consisted of a pound or more of small chips, which were for the most part light coloured, with here and there a slightly darker one. When examined with a pocket lens the stone appears made up of irregular rounded grains, some bright and translucent, others milky, many dark and opaque.

Quartzite is considered to be an altered sandstone, the alteration consisting in the cementation of the somewhat loose quartz grains of the sedimentary rock by transfusion of siliceous matter in solution. Heat and pressure, also, will doubtless have contributed not a little to bring about the change in physical character.

A friend, Mr. E. Dickson, to whom I showed the stone, selected a piece from which a section was afterwards cut for microscopical examination. He says of the rock:—"It is a compact felspathic quartzite. When examined microscopically there are evidences of a third mineral, but owing to the decomposed condition of the felspar and this mineral in the specimen examined it is almost im-

possible to determine them accurately. The felspar is, however, most probably orthoclase. The section shows presence of iron. Under a ¼ objective both the quartz and the felspar, but more especially the former, are seen to contain cavities, some being relatively of large size. The quartz grains clearly indicate the clastic character of the rock. They also exhibit secondary enlargement, due to infiltration of silica; the interstices of the rock have in this way become filled with silica not in optical continuity with that of the original grains."

The object is seen to great advantage under a binocular with an inch power, the granules many of them appearing to shade off into adjoining ones, merging their identity in that of their neighbours. When viewed as above a large number of the grains are seen to be speckled throughout with finely divided dark matter. As regards the cavities I am able to confirm Mr. Dickson's observation. A photo-micrograph was taken of the section, which is interesting to study. The accompanying illustration is from a pencil-sketch with the camera lucida, and has a magnification of 55 diameters.

Pontesbury Quartzite. (Magnification 55 linear).

A chemical analysis of a uniform sample of the quartzite was made, in which I employed both the fusion and HF methods of treatment. The following numbers were obtained:—

| | |
|---|---|
| $SiO_2$ .. .. .. .. | 94·850 |
| $Al_2O_3$ .. .. .. .. | 2·380 |
| $Fe_2O_3$ .. .. .. .. | 0·619 |
| $K_2O$ .. .. .. .. | 0·668 |
| $Na_2O$ .. .. .. .. | 0·712 |
| Carbon .. .. .. | 0·070 |
| Combined water .. | 0·627 |
| | 99·926 |

The combined water was found by direct weighing, and is the mean of two estimations.

Four were made of the alkalies; two by L. Smith's plan, and two by use of HF in solution.

It was when treating the quartzite with a re-distilled solution of HF that the carbon was first detected. The fact of the insoluble matter being chiefly carbon was established later on. In some of the slightly darker fragments of the stone—which I should state were washed with a clean brush and water only, and then dried—the carbon amounted to 0·13 per cent.

Is this carbon in the quartzite traceable to organic remains in the sedimentary rock before this rock was metamorphosed into quartzite?

The finding of carbon in the latter seems to point to the existence of organised forms in Cambrian or pre-Cambrian times, and supports the evidence of the supposed fucoid markings and worm-tracks found in the quarry whence this stone was obtained.

## DETECTION OF BLOOD-SPOTS IN PRESENCE OF IRON-RUST.

By E. DANNENBERG.

Generally speaking the detection of blood in chemico-legal investigations has not been difficult since the discovery of the crystals of hæmine. The case is different if blood-spots fall upon rusty iron, in which case no hæmine crystals can be produced, since the blood becomes insoluble in consequence of its combination with ferric oxide. Setting out with the idea of decomposing the compound of blood and iron by means of alkaline sulphides, the author obtained in a preliminary experiment, from a mixture of about equal parts of blood, water, and ammonium sulphide (according to Erdmann's process), along with the ordinary hæmine crystals, a number of others hitherto unknown. They were very elegant, extended, rhombic tables, brown, but with a clear colourless portion or stripe in the direction of the minor diameter of the rhombus. Some of them were rhomboidal or had blunted ends, but there was always the clear stripe in the middle.

These "hæmadine" crystals are obtained with such certainty from blood-stained rust that in thirty experiments, with strong and slight spots, the author was always successful. He proceeds as follows:—He lets fall upon the suspected spot, according to its size, two, four, or six drops of a 10 per cent solution of caustic potash, and lets

it soak for an hour. The spot is then loosened with a knife-point, and rinsed into a small porcelain capsule, in whioh it is repeatedly washed by decantation, removing the water at last almost entirely by inclining the capsule. The residue is moistened with a few drops of ammonium sulphide, rubbing the mass up with a pestle, and applying a gentle heat. In about ten minutes it is diluted with a little water and filtered. The first few drops, if treated according to Erdmann's process, yield the new hæmadine crystals.—*Chemiker Zeitung.*

(Dr. Amtha maintains that these crystals are merely sulphur, and that they can be obtained in the absence of blood.)

## FURTHER RESEARCHES ON COMPLEX INORGANIC ACIDS.

By DR. WOLCOTT GIBBS.

You will doubtless remember the very interesting and curious results obtained many years since by Schützenberger by the action of phosphoric pentachloride upon spongy platinum. We have simply $Pt + PCl_5 = PtCl_2.PCl_3$, the compound by the action of water giving the corresponding acid $PtCl_2.P(OH)_3$. A second and analogous compound chloride has the formula $PtCl_2.2PCl_3$, and this yields the acid $P_2.PtCl_2.(OH)_6$. A third acid has the formula $P_2.PtCl_2.(OH)_5$, and a fourth is represented by $P_2O_2.PtCl.(OH)_3$. These compounds have attracted very little attention, perhaps on account of the neglect and contempt into which inorganic chemistry has fallen of late years. Schützenberger does not appear to have attempted to generalise his results. I have endeavoured to show, in a paper read before the National Academy of Science, that in Schützenberger's acids platinous chloride simply replaces an atom of oxygen, and that, by appropriate methods, we ought to be able to perform the inverse substitution and obtain three new acids of phosphorus which would have respectively the formulæ $P_2O(OH)_6$, $P_2O(OH)_5$ or perhaps $P_4O_2(OH)_{12}$, and $P_4O_7(OH)_6$, since $2PtCl''' = 3O$. Of course the first acid mentioned above, $P.PtCl_2.(OH)_3$, is, on this view, orthophosphoric acid, in which $PtCl_2$ replaces one atom of oxygen. I have now succeeded in generalising these results in what seems to me an interesting manner. In the first place I have discovered compound acids analogous to chlorplatinorthophosphoric acid which contain respectively palladium, iridium, ruthenium, and osmium in place of platinum. Want of material has prevented me from experimenting with rhodium also, but it can hardly be doubted that it forms similar compounds. In the next place I find that platinous chloride may be replaced by platinous oxide or bromide, and the same appears to be true for other metals of the platinum group. A still further generalisation consists in replacing phosphorus by arsenic and antimony, which is easily effected. It is to be expected that vanadium will yield similar compounds, but here again want of material has prevented the actual experiment up to the present time. The following formulæ, which are, I believe, to be depended on, will serve to illustrate my results:—

$$As_2O_3.3[As_2O_3.2PtO]5(NH_4)_2O + 7Aq.$$
$$[As_2O_3.2PtCl_2]K_2O.2H_2O.$$

As I have written it, the first compound might be called an arsenoso-oxyplatin-arsenate, and the second a chlorplatin-arsenate. When these compounds are digested or boiled with acid tungstates and molybdates, higher complex acids are obtained, which I am now studying. One tungsten compound appears to have the formula—

$$24WO_3.As_2O_3.3[As_2O_3.2PtCl_2]12Pt(NH_3)_4O + 60Aq.$$

Another, the formula—

$$22WO.3As_2O_3.3[As_2O_3.2PtO]6Pt(NH_3)_4O + 40Aq.$$

A beautiful pale green molybdenum compound has the formula—

$$12MoO_3.As_2O_3[As_2O_3.2PtO]2Pt(NH_3)_4O + 27Aq.$$

All these compounds contain the oxide of platinoditetramine, $Pt(NH_3)_4O$, as a base. The formulæ given, however, are only preliminary, and may hereafter prove reducible to simpler expressions. The salts were obtained by digesting or boiling the green salt of Magnus, $Pt(NH_3)_4Cl_2 + PtCl_2$, with arsenoso-tungstates and arsenoso-molybdates. Analogous series appear to be formed when arsenoso-phospho-tungstates and arsenoso-phospho-molybdates are digested or boiled with platinous chlorine or with the tetramine salt. Now, replace platinum by other metals of the same group, and arsenic by antimony or phosphorus, perhaps also by vanadium, and you will have some idea of the extent of the new field of work in which I am now labouring as fast as my limited means and resources will permit.—*American Chemical Journal*, vol. viii., No. 4.

## ANALYSES OF COMMERCIAL FERTILISERS.*

### Official Methods of the Association of Agricultural Chemists for 1886-7.

(Continued from p. 39.)

### Method for Determining Phosphoric Acid and Moisture.

(1) *Preparation of Sample.*—The sample should be well intermixed and properly prepared, so that separate portions shall accurately represent the substance under examination, without loss or gain of moisture.

(2) *Determination of Moisture.*—(*a.*) In potash salts, nitrate of soda, and sulphate of ammonia heat 1 to 5 grms. at 130° C. till the weight is constant, and reckon water from the loss. (*b.*) In all other fertilisers heat 2 grms., or, if the sample is too coarse to secure uniform lots of 2 grms. each, 5 grms. for five hours at 100° in a steam-bath.

(3) *Water-soluble Phosphoric Acid.*—Bring 2 grms. on a filter, add a little water, let it run out before adding more water, and repeat this treatment cautiously until no phosphate is likely to precipitate in the filter. If the washings show turbidity after passing the filter, clear up with acid. When the substance is nearly washed in this manner it is transferred to a mortar and rubbed with a rubber-tipped pestle to a homogeneous paste (but not further pulverised), then returned to the filter, and washed with water until the filtrate measures not less than 250 c.c. Mix the washings. Take an aliquot (usually corresponding to ½ or ½ grm. of the substance) and determine phosphoric acid, as under "Total Phosphoric Acid."

(4) *Citrate-insoluble Phosphoric Acid.*—Wash the residue of the treatment with water into a 150 c.c. flask with 100 c.c. of strictly neutral ammonium citrate solution of 1·09 density, shred and add the filter-paper, cork the flask securely, place in a water-bath with constant temperature of 65° C., and digest for thirty minutes at this temperature with frequent shaking; filter the warm solution quickly, and wash with water of ordinary temperature. Transfer the filter and its contents to a capsule, ignite until the organic matter is destroyed, treat with 10 to 15 c.c. of concentrated hydrochloric acid, digest over a low flame until the phosphate is dissolved, dilute to 200 c.c., mix, pass through a dry filter; take an aliquot, and determine phosphoric acid as under "Total."

In case a determination of citrate-insoluble phosphoric acid is required in non-acidulated goods, it is to be made by treating 2 grms. of the phosphatic material without previous washing with water, precisely in the way above

* From the *Proceedings* of the Third Annual Convention of the Association of Official Agricultural Chemists, at Washington, D.C., August 26 and 27, 1886. Edited by Clifford Richardson, Secretary.

described, except that in case the substance contains much animal matter (bone, fish, &c.) the residue insoluble in ammonium citrate is to be digested with HCl and $KClO_3$, as described below.

(5) *Total Phosphoric Acid.*—Weigh 2 grms. into a flask or beaker, add 30 c.c. concentrated hydrochloric acid, heat and add cautiously and in small quantities at a time about 0·5 grm. finely powdered potassium chlorate. Digest at a gentle heat until all phosphates are dissolved and all organic matter destroyed, dilute to 200 c.c., mix, pass through a dry filter; take 50 c.c. of filtrate, neutralise with ammonia; for every decigrm. of $P_2O_5$ that is present 50 c.c. of molybdic solution. Digest at about 65° C. for one hour, filter, and wash with ammonium nitrate solution. (Test the filtrate by renewed digestion and addition of more molybdic solution. Dissolve the precipitate on the filter with ammonia and hot water, and wash into a beaker to a bulk of not more than 100 c.c. Nearly neutralise with hydrochloric acid, cool, and add magnesia mixture from a burette: add slowly (one drop per second), stirring vigorously. After fifteen minutes add 30 c.c. of ammonia solution of density 0·95. Let stand several hours (two hours is usually enough). Filter, wash with dilute ammonia, ignite intensely for ten minutes, and weigh.

(6) *Citrate-soluble Phosphoric Acid.*—The sum of the water-soluble and citrate-insoluble subtracted from the total gives the citrate-soluble.

*Preparation of Reagents.*

(1) *To Prepare Ammonium Citrate Solution.*—Mix 370 grms. of commercial citric acid with 1500 c.c. of water; nearly neutralise with crushed commercial carbonate of ammonia, heat to expel the carbonic acid, cool, add ammonia until exactly neutral (testing by saturated alcoholic solution of coralline), and bring to volume of 2 litres. Test the gravity, which should be 1·09 at 20°, before using.

(2) *To Prepare Molybdic Solution.*—Dissolve 100 grms. of molybdic acid in 400 grms. or 417 c.c. of ammonia of sp. gr. 0·96, and pour the solution thus obtained into 1500 grms. or 1250 c.c. of nitric acid of sp. gr. 1·20. Keep the mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phospho-molybdate. Decant the solution from any sediment, and preserve in glass-stoppered vessels.

(3) *To Prepare Ammonium Nitrate Solution.*—Dissolve 200 grms. of commercial ammonium nitrate in water, and bring to a volume of 2 litres.

(4) *To Prepare Magnesia Mixture.*—Dissolve 22 grms. of recently-ignited calcined magnesia in dilute hydrochloric acid, avoiding excess of the latter. Add a little calcined magnesia in excess, and boil a few minutes to precipitate iron, alumina, and phosphoric acid; filter; add 280 grms. of ammonium chloride, 700 c.c. of ammonia of sp. gr. 0·96, and water enough to make the volume of 2 litres. Instead of the solution of 22 grms. of calcined magnesia, 110 grms. of crystallised magnesium chloride ($MgCl_2,6H_2O$) may be used.

(5) *Dilute Ammonia for Washing.*—One volume ammonia of sp. gr. 0·96 mixed with 3 volumes of water, or usually 1 volume of concentrated ammonia with 6 vols. of water.

Methods for Determining Potash.

In case the potash is contained in organic compounds like tobacco stems, cotton-seed hulls, &c., it is to be saturated with strong sulphuric acid and ignited in a muffle to destroy organic matter. Pulverise the fertiliser (200 or 300 grms.) in a mortar; take 10 grms., boil for ten minutes with 200 c.c. water, and after cooling, and without filtering, make up to 1000 c.c., and filter through a dry paper. If the sample have 10 to 15 per cent $K_2O$ (kainite), take 50 c.c. of the filtrate; if from 2 to 3 per cent $K_2O$ (ordinary potash fertilisers), take 100 c.c. of the filtrate. In each case make the volume up to 150 c.c., heat to 100°, and add, drop by drop, with constant stirring, slight excess of barium chloride; without filtering, in the same manner, add barium hydrate in slight excess. Heat, filter, and wash until precipitate is free of chlorides. Add to filtrate 1 c.c. strong ammonium hydrate, and then a saturated solution of ammonium carbonate until excess of barium is precipitated. Heat. Add now, in fine powder, 0·5 grm. pure oxalic acid, or 0·75 grm. ammonium oxalate. Filter, wash free of chlorides, evaporate filtrate to dryness in a platinum dish, and, holding dish with crucible tongs, ignite carefully over the free flame below red heat until all volatile matter is driven off.

The residue is now digested with hot water, filtered through a small filter, and washed with successive small portions of water until the filtrate amounts to 30 c.c. or more. To this filtrate, after adding two drops of strong hydrochloric acid, is added, in a porcelain dish, 5 to 10 c.c. of a solution of 10 grms. of platinic chloride in 100 c.c. of water. The mixture is now evaporated on the water-bath to a thick syrup, or further, treated with strong alcohol washed by decantation, collected in a Gooch crucible or other form of filter, washed with strong alcohol, afterwards with 5 c.c. ether, dried for thirty minutes at 100°, and weighed.

It is recommended that if there is an appearance of white foreign matter in the double salt it should be washed with 10 c.c. of a half-concentrated solution of $NH_4Cl$, which has been saturated by shaking with $K_2PtCl_6$, rejecting the first portion running through and using 10 c.c. of fresh solution, returning the same portion five or six times upon the salt, and finally using another portion, and then alcohol and ether, after the method recommended by Gladding.

As an alternative the entire method of Lindo, as modified by Gladding, may be used in the determination of potash when, in the opinion of the analyst, it is found satisfactory.

The use of the factor 0·3056 for converting $K_2PtCl_6$ to KCl and 0·19308 for converting to $K_2O$ are continued.

Method of Lindo as modified by Gladding.

(1) *Superphosphates.*—Boil 10 grms. of the fertiliser with 300 c.c. of water for ten minutes. Cool the solution, add ammonia in slight excess, thus precipitating all phosphate of lime, oxide of iron, alumina, &c.; make up to 500 c.c., mix thoroughly, and filter through a dry filter; take 50 c.c., corresponding to 1 grm., evaporate nearly to dryness, add 1 c.c. of dilute $H_2SO_4$ (1 to 1), and evaporate to dryness and ignite to whiteness. As all the potash is in form of sulphate, no loss need be apprehended by volatilisation of potash, and a full red heat must be used until the residue is perfectly white. This residue is dissolved in hot water plus a few drops of HCl; 5 c.c. of a solution of pure NaCl (containing 20 grms. NaCl to the litre) and an excess of platinum solution (4 c.c.) are now added, and the whole evaporated as usual. The precipitate is washed thoroughly with alcohol by decantation and on filter, as usual. The washing should be continued even after the filtrate is colourless. Ten c.c. of the $NH_4Cl$ solution prepared as above are now run through the filter. These 10 c.c. will contain the bulk of the impurities, and are thrown away. A fresh portion of 10 c.c. $NH_4Cl$ is now run through the filter several times (5 or 6). The filter is then washed thoroughly with pure alcohol, dried, and weighed as usual. The platinum solution used contains 1 grm. metallic platinum in every 10 c.c.

(2) *Muriates of Potash.*—In the analysis of these salts an aliquot portion, containing 0·500 grm., is evaporated with 10 c.c. platinum solution plus a few drops of HCl, and washed as before.

(3) *Sulphate of Potash, Kainite, &c.*—In the analysis of these salts an aliquot portion, containing 0·500 grm. is taken, 0·250 grm. of NaCl added, plus a few drops of HCl, and the whole evaporated with 15 c.c. platinum solution. In this case special care must be taken, in the

washing with alcohol, to remove all the double chloride of platinum and sodium. The washing should be continued for some time after the filtrate is colourless. Twenty-five c.c. of the $NH_4Cl$ solution are employed instead of 10 c.c., and the second 25 c.c. poured through at least six times to remove all sulphates and chlorides. Wash finally with alcohol, dry, and weigh as usual.

To prepare the washing solution of $NH_4Cl$, place in a bottle 500 c.c. $H_2O$, 100 grms. of $NH_4Cl$; shake till dissolved. Now pulverise 5 or 10 grms. of $K_2PtCl_6$, put in the bottle, and shake at intervals for six or eight hours; let settle over night; then filter off liquid into a second bottle. The first bottle is then ready for a preparation of a fresh supply when needed.

### Determination of Nitrogen by the Absolute or Cupric Oxide Method.

The apparatus and reagents needed are as follows:—

#### *Apparatus.*

*Combustion tube* of best hard Bohemian glass, about 26 inches long and ¼ inch internal diameter.

*Azotometer* of at least 100 c.c. capacity accurately calibrated.

*Sprengel mercury air-pump.*

*Small paper scoop*, easily made from stiff writing-paper.

#### *Reagents.*

*Cupric Oxide* (coarse).—Wire form; to be ignited and cooled before using.

*Fine Cupric Oxide.*—Prepared by pounding ordinary cupric oxide in mortar.

*Metallic Copper.*—Granulated copper or fine copper gauze reduced and cooled in stream of hydrogen.

*Sodium Bicarbonate.*—Free from organic matter.

*Caustic Potash Solution.*—Dissolve commercial stick potash in less than its weight of water, so that crystals are deposited on cooling. When absorption of carbonic acid ceases to be prompt, solution must be discarded.

#### *Loading Tube.*

Of ordinary commercial fertilisers take 1 to 2 grms. for analysis. In the case of highly nitrogenous substances the amount to be taken must be regulated by the amount of nitrogen estimated to be present. Fill tube as follows: (1) About 2 inches of coarse cupric oxide. (2) Place on the small paper scoop enough of the fine cupric oxide to fill, after having been mixed with the substance to be analysed, about 4 inches of the tube; pour on this the substance, rinsing watch-glass with a little of the fine oxide, and mix thoroughly with spatula; pour into tube, rinsing the scoop with a little fine oxide. (3) About 12 inches of coarse cupric oxide. (4) About 3 inches of metallic copper. (5) About 2½ inches of coarse cupric oxide (anterior layer). (6) Small plug of asbestos. (7) Eight-tenths to 1 grm. of sodium bicarbonate. (8) Large loose plug of asbestos; place tube in furnace, leaving about 1 inch of it projecting; connect with pump by rubber stopper smeared with glycerin, taking care to make connection perfectly tight.

#### *Operation.*

Exhaust air from tube by means of pump. When a vacuum has been obtained allow flow of mercury to continue; light gas under that part of tube containing metallic copper, anterior layer of cupric oxide (see 5th above), and bicarbonate of soda. As soon as vacuum is destroyed and apparatus filled with carbonic acid gas, shut off the flow of mercury, and at once introduce the delivery tube of the pump into the receiving arm of the azotometer and just below the surface of the mercury seal of the azotometer, so that the escaping bubbles will pass into the air and not into the azotometer, thus avoiding the useless saturation of the caustic potash solution.

When the flow of carbonic acid has very nearly or completely ceased, pass the delivery tube down into the receiving arm so that the bubbles will escape into the azotometer. Light the jets under the 12-inch layer of oxide, heat gently for a few moments to drive out any moisture that may be present, and bring to red heat. Heat gradually mixture of substance and oxide, lighting one jet a time. Avoid too rapid evolution of bubbles, which should be allowed to escape at the rate of about one per second, or a little faster.

When the jets under mixture have all been turned on, light jets under layer of oxide at end of tube. When evolution of gas has ceased, turn out all the lights except those under the metallic copper and anterior layer of oxide, and allow to cool for a few moments. Exhaust with pump, and remove azotometer before flow of mercury is stopped. Break connection of tube with pump, stop flow of mercury, and extinguish lights. Allow azotometer to stand for at least an hour, or cool with stream of water until permanent volume and temperature are reached.

Adjust accurately the level of the KOH solution in bulb to that in azotometer,; note volume of gas, temperature. and height of barometer; make calculations as usual. The labour of calculation may be much diminished by the use of the tables prepared by Messrs. Battle and Dancy, of the North Carolina Experiment Station (Raleigh, N.C.).

The above details are, with some modifications, those given in the Report of the Connecticut Station for 1879 (p. 124), which may be consulted for details of apparatus, should such details be desired.

(To be continued.)

## LONDON WATER SUPPLY.

### Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month ending December 31st, 1886.

By WILLIAM CROOKES, F.R.S.,

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
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and C. MEYMOTT TIDY, M.B., F.C.S.,
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*To* Colonel Sir Francis Bolton, *Water Examiner, Metropolis Water Act*, 1871.

London, January 7th, 1887.

Sir,—We submit herewith the results of our analyses of the 165 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from December 1st to December 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Altogether, the December supply of water to the Metropolis compares, in some respects, a little unfavourably with that furnished, with such marked invariability of character, for now many months past. The increase in the proportion of organic matter present in the water, as determined alike by the combustion process and the oxygen-absorption process, is, however, quite insignificant; the mean amount of organic carbon, for instance,

in the Thames-derived supply, being 0·170 part in 100,000 parts of the water, as against a mean of 0·167 part in November, and a mean of 0·137 part in the preceding four months. But, as shown in Table II., the supplies furnished by two of the seven companies during the latter half of the month, were occasionally not free from turbidity,—no single instance of even slight turbidity having been met with among the 910 samples examined in the course of the preceding five months; neither was the water, during the latter part of the month, so uniformly free from other than a preponderating blue tint of colour.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

## ON THE ANALYSIS OF OPIUM.

By CHARLES M. STILLWELL, M.A.

(Concluded from p. 43).

*Filtering off the Aqueous Solution of Morphia.*—Filter off the solution into a graduated cylinder, and wash the filter and residue with water applied from a wash-bottle until the filtrate measures about 120 c.c.; set this strong solution aside, and return the residue to the bottle or beaker by means of a small spatula; add 30 c.c. of water, and mix or shake well, and filter this solution through the same filter. Again return the residue and treat with 20 c.c. of water and filter, and finally repeat the treatment with 20 c.c. more. By the use of the rubber-tipped rod and a beaker it is possible to so press out the water from the insoluble residue that the above treatment will exhaust 10 grms. of any opium. The water is much more thoroughly obtained from the residue than by using several more washings without pressure. It is best to let the several washings stand on the residue for ten minutes or so before transferring to the filter. These washings are received in a beaker, and are the first portion to be evaporated.

*Evaporation of the Aqueous Solution of Morphia.*—The second portion of the solution, the washings, measuring about 70 c.c., is placed in a porcelain capsule of 6 to 8 inches diameter, and evaporated over a water-bath at a heat below boiling. By using a broad shallow dish this evaporation takes little time, and the danger of injury to the alkaloid is reduced to a minimum. Evaporate to about 25 c.c. and then add the first portion of the solution, washing out the cylider with a little water from the wash-bottle, and evaporate the whole to about 25 c.c. Cool the capsule and contents and add 5 c.c. of alcohol (sp. gr. 0·820), and stir until a uniform solution is obtained. If a precipitate is obtained, as sometimes happens, it is not necessary to filter, as this precipitate is removed in a subsequent treatment, and is not reckoned as morphia.

*Transferring to the Crystallising Flask.*—Pour the solution into an Erlenmeyer flask fitted with a good velvet cork, using a flask of about 2 inches diameter at the bottom and 5 inches high, and wash the capsule with about 5 to 10 c.c. of water from the wash-bottle. I find that the quantities of water for washing and for the precipitation of the morphia may be slightly greater than those recommended by Dr. Squibb, without injury to the analysis. Add 5 c.c. more of alcohol, and mix the liquids thoroughly by rotating the flask, and not by an up and down movement. Then add 30 c.c. ether and again mix well by rotating.

"This shaking together first of the watery solution and alcohol causes the alcohol to combine with the water before the ether is added. The ether then added, the second shaking saturates the watery solution and combined alcohol with ether, and then the mixture is ready for the precipitation of the alkaloid under the most favourable conditions."*

*Precipitation of the Morphia.*—Add 40 c.c. of ammonia solution of 10 per cent (sp. gr. 0·960), wet the cork with ether, and insert at once into the flask. Shake the flask *strongly* with an up and down motion until the crystals begin to separate. This will occur in a moment or two if everything has been properly carried out. Then set the flask aside for twelve hours, or over night, to complete the crystallisation. By this vigorous shaking the crystals are obtained in a fine granular condition, easily washed and separated from the flask.

*Filtering off the Morphia.*—"Pour off the ethereal stratum from the flask as closely as possible on to a tared filter of about 10 c.=4 inches in diameter, well wetted with ether. Add 20 c.c. of ether to the contents of the flask, rinse round without shaking, and again pour off the ethereal stratum as closely as possible on to the filter, keeping the funnel covered. When the ethereal solution is nearly all through, wash down the edges and sides of the filter with 5 c.c. of ether, and allow the filter to drain with the cover off. Then pour on the remaining contents of the flask, and cover the funnel. When the liquid has nearly all passed through, rinse the flask twice with 5 c.c. of water each time, pouring the rinsings with all the crystals that can be loosened on to the filter, and dry the flask in an inverted or horizontal position, and when thoroughly dry, weigh it. Wash the filter and crystals with 10 c.c. of water applied drop by drop to the edges of the filter. When drained, remove the filter and contents from the funnel, close the edges of the paper together, and compress it gently between many folds of bibulous paper. Then dry it at 100° C., and weigh it. Remove the crystals of morphia from the filter, brush it off, and re-weigh it to get the tare to be subtracted. The remainder, added to the weight of the crystals in the flask, will give the total yield of morphia in clean, distinct, small, light brown crystals.

"Take a small portion of these crystals, rub them into very fine powder, and weigh off 0·1 grm. Put this in a large test-tube fitted with a good cork, and add 10 c.c. of officinal lime water. Shake occasionally, when the whole of the powder should dissolve. (Absence of Narcotine: Flückiger.)

". . . This process, according to the skill and care with which it is managed, will give uniform results to within two or three-tenths of a per cent. Adulterated opiums are much more difficult to assay, and yield crystals which are always darker and less clean, and, therefore, the results are almost always too high. Poor opiums, on the other hand, are very easy to assay, and usually give very light-coloured clean morphia. The results here are liable to be too low, because, when the quantity of morphia is small, the alcohol and ammonia used are proportionally too large, so that much morphia may be retained in the mother-liquor. Therefore, when the morphia comes out very white and in small proportion, the assay should always be repeated, evaporating the solution to 10 grms. instead of 20, and adding 5 c.c. of alcohol instead of 10, and 2·5 or 3 c.c. of ammonia instead of 4. . . .

"The above process is very easily applicable to the assay of such preparations of opium as the tincture, deodorised tincture, and compound solution. For the assay of these—

"Take of the liquid preparation 120 c.c. Evaporate at a low temperature to 10 grms., and from this point proceed exactly as in the above process, using, however, 5 c.c. of alcohol instead of 10, and 2·5 to 3 c.c. of ammonia instead of 4."†

In following out the above plan of Dr. Squibb, several difficulties are met with. The amount of ether recommended for washing is so small that in some cases where the operation of filtering proceeds with great difficulty,

* *Ephemeris*, i., 17.
† *Ibid.*, i., 17, 20.

much of the ethereal solution is evaporated from the edges of the filter-paper, leaving its contents behind, and these are not thoroughly washed out by the subsequent treatment. The amount of water, also, is too small to allow of perfect washing.

*Washing Solutions.*—In order to obviate these difficulties I have adopted a plan for which I am indebted to a paper published by E. F. Teschemacher, F.C.S., &c., in the Chemical News, vol. xxxv., p. 47. The first solution, which he calls "*Morphiated Spirit*," is made by mixing one part of ammonia solution, sp. gr. 0·880, with twenty parts of alcohol, and digesting in this mixture, for several days, a large excess of morphia. The clear solution will contain 0·33 per cent of morphia. The second solution, called "*Morphiated Water*," is water saturated by long shaking with morphia. The filtered solution contains 0·04 per cent morphia.

By washing with these solutions the extractive matter is completely removed from the filter-paper and crystals of morphia. I prefer to use balanced filter-papers of $4\frac{1}{2}$ inches diameter. The solution is run through one of these, and, by means of the thorough washing with the solutions above described, the two papers are left, at the end of the operation, ready for weighing against each other as at first. I pour off the ethereal stratum through the filter as above described, and then wash several times with 10 c.c. of ether, rinsing the flask around without shaking, and letting settle for a few minutes. Even if a small amount of the ethereal residue is left upon the paper by evaporation, it is immatetial, as in the subsequent treatment this is removed. A small syphon is advantageously used to draw off the ethereal solution from the Erlenmeyer flask, but if an attempt be made to syphon off the ethereal washings, it will be found that the bubbles formed in the ether collect in the tube of the syphon and prevent its action, so that it is better to wash by decantation. If some of the aqueous solution pass into the filter with the ether it is of no importance. The washing with ether is followed, first, by a thorough washing with the "*Morphiated Spirit*," thus removing all the colouring matter and resin soluble in this menstruum, and then by a thorough washing with the "*Morphiated Water*," until the filtrate comes through colourless and the paper shows by its colour that all the extractive matter is removed. By the use of the Erlenmeyer flask it is possible to remove with the rubber-tipped rod all the crystals from the flask, so that no drying and weighing of the flask is needed. After the washing with the "*Morphiated Water*" the filter is left to drain for a few minutes in the funnel, and two washings of 10 c.c. each with the "*Morphiated Spirit*" are given. This removes the bulk of the water from the paper and crystals. Let drain for a few minutes, keeping the funnel covered with a watch-glass, and then wash twice with 10 c.c. each time of ether. This will remove any narcotine which may have been left from the evaporation of the ethereal solution at the beginning of the operation. The paper and contents are thus left in a condition to be rapidly dried. Let the filter and its contents stand exposed for a few minutes, and then dry it at 100° C. and weigh. Twenty minutes or half an hour's drying is usually sufficient.

On account of the removal of the water it is possible to dry the filter and its contents in a short time at a much lower temperature than 100° C., but as it is easier to employ this heat, and no decomposition of the morphia crystals occurs, I use it. A precipitate of morphia crystals was dried for two hours at 60° C., yielding a weight of 1·306 grms. It was further dried for three hours at the same heat and then weighed 1·305 grms.; still further dried for two hours at 100° C., it became 1·301 grms.

The mother-liquor, together with the first washings of ether and "*Morphiated Spirit*," is put in a flask, 3 c.c. of ammonia added, and the corked flask is set aside over night in order to see if a further crystalline precipitate of morphia occur. If the solution is left exposed in an open beaker, amorphous flakes will settle out, consisting chiefly of resinous matter, very different from the heavy crystalline deposit of morphia.

Having thus obtained the weight of the crystalline precipitate, it is still necessary to further purify it before the final calculation is made for the per cent. The precipitate of morphia obtained by Dr. Squibb's process contains insoluble matter, resinous and other organic matters soluble in alcohol, and meconate of lime, the latter constituting about 25 per cent of the impurities present. The average amount of the impurities present in the crystals obtained by his process is 8 per cent of the weight of the crystals. The meconate of lime extracted by the acid solution of the opium is retained in solution until the addition of the ammonia, when it is precipitated with the crystals of morphia, and remains with them until the final weighing. The resinous and other organic matters, insoluble in water, but soluble in alcohol, are not thoroughly removed with the limited washing given in his process, and no provision is made for their subsequent removal. The thorough washing with "*Morphiated Spirit*" which I employ takes out these substances, and the subsequent treatment with "*Morphiated Water*" removes those insoluble in alcohol, so that the chief impurity present in the crystals of morphia obtained by my modification of the process is meconate of lime, together with some organic matters insoluble in water and alcohol.

*Purification of the Precipitate.*—After drying and weighing the crystals they are carefully rubbed or brushed from the filter, the latter being then placed in a funnel and preserved with its balanced paper for future use. The precipitate is treated in a small beaker with hot alcohol of 95 per cent. This dissolves all the morphia, leaving the insoluble organic matter and meconate of lime. The hot alcoholic solution is run through the filter which contained the morphia, the small portion of the crystals remaining on the paper being thus drenched with hot alcohol and the morphia dissolved. This treatment with hot alcohol is continued until all the morphia is dissolved. This extraction with alcohol may be done in a Soxhlet's apparatus, if desired. The filter is then dried with its balanced paper and the amount of residue obtained. This is subtracted from the original weight of the precipitate, and the remainder calculated into the per cent of morphia. The alcoholic solutions of morphia are placed in a bottle and left to deposit the excess of morphia, and the alcohol, saturated with morphia, is used for the preparation of the "*Morphiated Spirit*" as before described. Meconate of lime I found to be perfectly insoluble in boiling alcohol. A long treatment with this solvent failed to dissolve enough meconate of lime to give a trace of colour with ferric salts.

The composition of the morphia crystals, on which the calculation for the per cent is based, is $C_{34}H_{19}NO_6+2Aq$, containing 5·94 per cent of water of crystallisation. At 120° C. the water is expelled, and at a higher temperature the crystals become carbonised.

The following is a brief summary of my process as practised in our laboratory.

1. *Sampling.*—By taking a portion of every tenth lump in a case.

2. *Preparation of the Sample.*—By thorough mixing of the small samples obtained, either by kneading or rolling, or by drying the sample, with previous estimation of the water.

3. *Extraction of the Morphia.*—Weigh off about 10 grms., noting the exact weight taken; treat with 100 c.c. of water in a suitable vessel, macerate, let stand over night, filter, and wash, making two portions of the filtrate. Evaporate on a water-bath, first the weaker portion, about 70 c.c. of solution, then add the stronger portion, and evaporate all to 25 c.c.; add 5 c.c. of alcohol and stir untill all is dissolved.

4. *Precipitation of the Morphia.*—Transfer the solution to a suitable flask, add 5 c.c. more of alcohol, mix; then add 30 c.c. of ether, mix; then add 4 c.c. of a 10 per cent

solution of ammonia, sp. gr. 0·960. Shake violently until the crystals form, and let stand over night.

5. *Filtration of the Morphia.*—Filter off, first, the ethereal solution and wash well with ether. Then filter the aqueous solution, and wash, first with "*Morphiated Spirit*," then with "*Morphiated Water*," then with "*Morphiated Spirit*," and finally with ether. Dry at 100° C. and weigh, using balanced papers.

6. *Purification of the Morphia.*—Treat the impure precipitate with hot alcohol until all the morphia is dissolved. Wash thoroughly with hot alcohol, dry, and weigh the insoluble residue. Subtract this from the first weight of the precipitate to get the amount of morphia present.

7. *Statement of the Result.*—Give the percentage of moisture present at 100° C., and of morphia, both on a wet and dry basis, in terms of crystallised morphia, $C_{34}H_{19}NO_6+2Aq$, dried at 100° C.

*Washing Solutions.*

*a.* "*Morphiated Spirit.*"—This is made by mixing one part of ammonia solution, sp. gr. 0·880, with twenty parts of alcohol and saturating with morphia. The filtered solution contains 0·33 per cent of morphia.

*b.* "*Morphiated Water.*"—This is made by saturating water by long shaking with excess of morphia. The filtered solution contains 0·04 per cent of morphia.

*c. Ether.*—Called stronger ether, sp. gr. 0·728 at 15·5° C.—*American Chemical Journal*, vol. viii., No. 5.

## A METHOD FOR THE SEPARATION OF SODIUM AND POTASSIUM FROM LITHIUM BY THE ACTION OF AMYL ALCOHOL ON THE CHLORIDES,

### WITH SOME REFERENCE TO A SIMILAR SEPARATION OF THE SAME FROM MAGNESIUM AND CALCIUM.*

By F. A. GOOCH.

(Continued from page 41.)

THE point of difference between these two series of experiments is the amount of lithium chloride introduced, only a tenth of that used in the former being employed in the latter. It is plain that, when we are dealing with the larger amount, a larger portion tends to remain behind with the insoluble chloride; and here again we meet, though to a degree comparatively harmless, the inclination of lithium chloride to yield chlorine and pass to the form of lithium hydrate. When the lithium chloride is present in small amount, as in the latter group of experiments, there can be little left undissolved; and the spectroscope confirms the evidence of the figures of analysis as to the perfectness of the separation, by showing in such cases either no lithium at all or merely fugitive traces. If a single precipitation is sufficient to effect a satisfactory separation of the insoluble chlorides from small amounts of lithium chloride, it is natural to suppose that a repetition of the precipitation would be beneficial in treating larger quantities of lithium chloride. Experiments (32) to (37) illustrate the effect of a double precipitation. The chlorides were brought to filtration as before, the liquid was decanted as completely as possible, the precipitate washed slightly by decantation and re-dissolved in a little water, and the round of boiling, filtering, drying, and weighing carried to the end as before, care being taken to repeat the treatment with a drop of hydrochloric acid during the process of boiling. The two portions of residual amyl alcohol were measured apart, as well as the washings (See Table below).

Thus it appears that, in the separation of the insoluble chlorides from the larger amounts of lithium chloride, the residue of two precipitations is substantially free from lithium.

For the sake of bringing the data in hand more directly into comparison, the corrected errors of the preceding determinations are tabulated again in the following statement (See Table next page).

Few processes in analytical chemistry are capable of yielding results more exact than these. The separation of from 0·1 grm. to 0·2 grm. of sodium or potassium chloride from a tenth of its own weight of lithium chloride is practically perfect in one operation, and from its own weight of lithium chloride the parting may be effected satisfactorily by two precipitations.

The points to be observed in executing the method may be recapitulated as follows:—

To the concentrated solution of the chlorides, amyl alcohol is added and heat is applied, gently at first to avoid danger of bumping, until the water disappearing

* *Proceedings of the American Academy of Arts and Sciences*, 1886-1887.

| | Weight of NaCl taken. | Weight of NaCl found. | Corrected weight of NaCl found. | Error in weight of NaCl found. | Error in corrected weight of NaCl found. | Volume of amyl alcohol used. Residual. I. | Residual. II. | Total. |
|---|---|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | Grm. | C.m.³ | C.m.³ | C.m.³ |
| (32) | 0·1166 | 0·1163 | 0·1169 | 0·0003 − | 0·0003 + | 8 | 8 | 150 |
| (33) | 0·1139 | 0·1127 | 0·1132 | 0·0012 − | 0·0007 − | 5 | 7 | 150 |

| | Weight of LiCl taken. | Weight of $Li_2SO_4$ found. | Weight of LiCl found. | Corrected weight of LiCl found. | Error in weight of LiCl found. | Error in corrected weight of LiCl found. |
|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | Grm. | Grm. |
| (32) | 0·1287 | 0·1662 | 0·1284 | 0·1280 | 0·0003 − | 0·0007 − |
| (33) | 0·1347 | 0·1759 | 0·1359 | 0·1353 | 0·0012 + | 0·0006 + |

| | Weight of KCl taken. | Weight of KCl found. | Corrected weight of KCl found. | Error in weight of KCl found. | Error in corrected weight of KCl found. | Volume of amyl alcohol used. Residual. I. | Residual. II. | Total. |
|---|---|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | Grm. | C.m.³ | C.m.³ | C.m.³ |
| (34) | 0·1155 | 0·1142 | 0·1152 | 0·0013 − | 0·0003 − | 10 | 10 | 100 |
| (35) | 0·1034 | 0·1017 | 0·1028 | 0·0017 − | 0·0007 − | 10 | 12 | 200 |
| (36) | 0·1914 | 0·1905 | 0·1912 | 0·0009 − | 0·0002 − | 3 | 11 | 90 |
| (37) | 0·1953 | 0·1939 | 0·1950 | 0·0014 − | 0·0003 − | 4 | 18 | 110 |

| | Weight of LiCl taken. | Weight of $Li_2SO_4$ found. | Weight of LiCl found. | Corrected weight of Li Cl found. | Error in weight of LiCl found. | Error in corrected weight of LiCl found. |
|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | Grm. | Grm. |
| (34) | 0·1125 | 0·1475 | 0·1139 | 0·1128 | 0·0014 + | 0·0003 + |
| (35) | 0·1251 | 0·1649 | 0·1274 | 0·1162 | 0·0023 + | 0·0011 + |
| (36) | 0·1263 | | — | — | — | — |
| (37) | 0·1282 | — | — | — | — | — |

| No. Exp. | Chloride. | Corrected Error of Insoluble Chloride: Precipitated *once* from about 0·13 grm. of LiCl. | Precipitated *once* from about 0·013 grm. of LiCl. | Precipitated *twice* from about 0·13 grm. of LiCl. | Error in corrected weight of LiCl. | Approximate mean error of LiCl. |
|---|---|---|---|---|---|---|
| | | Grm. | Grm. | Grm. | Grm. | Grm. |
| (23) | NaCl | 0·0006+ | — | — | 0·0002− | 0·0005+ |
| (24) | ,, | 0·0006+ | — | — | 0·0002− | |
| (26) | KCl | 0·0002+ | — | — | 0·0008− | |
| (27) | ,, | 0·0010+ | — | — | 0·0010− | |
| (25) | NaCl | — | 0·0000 | — | — | |
| (28) | KCl | — | 0·0005− | — | — | |
| (29) | ,, | — | 0·0004− | — | — | |
| (30) | NaCl+KCl | — | 0·0000 | — | — | |
| (31) | ,, ,, | — | 0·0007+ | — | — | |
| (32) | NaCl | — | — | 0·0003+ | 0·0007− | 0·0003− |
| (33) | ,, | — | — | 0·0007− | 0·0006+ | |
| (34) | KCl | — | — | 0·0003− | 0·0003+ | |
| (35) | ,, | — | — | 0·0007− | 0·0011+ | |
| (36) | ,, | — | — | 0·0002− | — | |
| (37) | ,, | — | — | 0·0003− | — | |
| | Approximate mean, | 0·0006+ | 0·00004− | 0·0003− | | |

from solution and the point of ebullition rising and becoming constant for some minutes at a temperature which is approximately that at which the alcohol boils by itself, the chlorides of sodium and potassium are deposited and lithium chloride is dehydrated and taken into solution. At this stage in the operation the liquid is cooled and a drop or two of strong hydrochloric acid added to re-convert traces of lithium hydrate in the deposit, and the boiling continued until the alcohol is again free from water. If the amount of lithium chloride present is small it will now be found in solution, and the chlorides of sodium and potassium will be in the residue, excepting the traces, for which correction will be made subsequently. If, however, the weight of lithium chloride present exceeds ten or twenty m.grms., it is advisable at this point, though not absolutely essential to the attainment of fairly correct results, to decant the liquid from the residue, wash the latter a little with anhydrous amyl alcohol, dissolve in a few drops of water, and repeat the separation by boiling again in amyl alcohol. For washing, amyl alcohol previously dehydrated by boiling is to be used, and the filtrates are to be measured apart from the washings. In filtering it is best to make use of the perforated crucible and asbestos felt, and apply gentle pressure. The crucible and residue are ready for the balance after drying for a few minutes directly over a flame turned low. The weight of insoluble chlorides actually obtained in this manner is to be corrected by the addition of 0·00041 grm. for every 10 c.m.$^3$ of amyl alcohol in the filtrate exclusive of washings if the insoluble salt is entirely sodium chloride, 0·00051 grm. for every 10 c.m.$^3$ if potassium chloride constitutes the residue, and if both sodium and potassium chloride are present, 0·00092 grm. ; but, as in the experiments described, the entire correction may in any case be kept within narrow limits, if due care be given to the reduction of the volume of residual alcohol before filtration. The filtrate and washings are evaporated to dryness, treated with sulphuric acid, the excess of the latter driven off, and the residue ignited to fusion and weighed. From the weight thus found the subtraction of 0·00050 grm. is to be made if sodium chloride constitutes the precipitate, 0·00059 grm. if potassium chloride alone is present in the residue, and 0·00109 if both of these chlorides are present, for every 10 c.m.$^3$ of filtrate exclusive of washings.

Amyl alcohol is not costly, the manipulations of the process are easy, and the only objectionable feature—the development of the fumes of amyl alcohol—is one which is insignificant when good ventilation is available.

The process has been used for some months frequently and successfully, by others as well as myself, for the estimation of lithium in waters and minerals.

To be continued).

## NOTICES OF BOOKS.

*Report on the Waters of the Hudson River, together with an Analysis of the Same, made to the Water Commissioners of the City of Albany.* By O. F. Chandler, Ph.D. January, 1885. New York: Trows.

This report gives, upon the whole, a favourable account of the Hudson River, as being, in purity, little inferior to the Croton. The total mineral matter is given as 8·313 grains per U.S. gallon of 231 cubic inches, the weight of this quantity being, unfortunately, not stated. He considers that rivers polluted with sewage are capable of self-purification by natural processes, except the impurities are introduced in immoderate quantities. He upholds chemical analysis as the means for determining the safety or danger of a water-supply. He does not indeed contend that chemistry can discriminate between pathogenic or septic microbia and such as are harmless, but he maintains that whenever mischief has been traced to a water, such water presented features which would ensure its condemnation on chemical principles. He has only a very qualified faith in the conclusiveness of biological and microscopical examination, on account of the practical omnipresence of the germs of bacteria. He writes that "when the biologist learns to detect in water the specific poisons of zymotic diseases and to distinguish them from the harmless organisms that we eat, drink, and breathe with impunity all our lives, then we may set up biological analysis as superior to chemical analysis." He supports these views by quotations from the late R. Angus Smith, Letheby, and Pettenkofer. Says the last-mentioned authority, "while Koch was in Calcutta the English physicians imbued him with their views on cholera and drinking-water. The English had been brought up on the drinking-water theory of typhoid fever and cholera, and could only lay it aside with difficulty."

In conclusion he maintains that the Hudson River furnishes a pure and safe water for the city of Albany, and that it would be foolish to incur heavy expenditure in introducing a new supply. The causes of zymotic disease, it is to be feared, are not quite so simple as it has been imagined, and we cannot hope to overcome them by the expedient of a pure water supply.

*Index to the Literature of Explosives* (Part I.). By Charles E. Munroe, S.B. (Harv.), Professor of Chemistry, U.S. Naval Academy. 1886. Baltimore: Isaac Friedenwald.

This index is intended to embrace not only such articles as treat of the composition and of the chemical and physical properties of explosive substances, but also of their manu-

facture and use in the arts. This part contains the titles of papers appearing in such periodicals as the indexer has been able to review from the date of first issue. 442 volumes have been thus reviewed for this part. Many other titles of papers have been collected, but the indexer has not yet had access to complete sets of the periodicals from which they have been gathered. A large number of titles of separate publications, treatises, text-books, and the like have also been collected. It is hoped that it will be possible to eventually publish these, together with a "subject" and "author's" index to the entire list.

## CORRESPONDENCE.

### ALKALI—CALIFORNIA.

*To the Editor of the Chemical News.*

Sir,—During my residence in California I had continual occasion to observe the effect of alkali in the soil. So pernicious is this substance that immense tracts of land lie uncultivated that would otherwise be covered with fruit trees or corn.

This efflorescence makes its appearance on the surface after rain or irrigation like snow, on loose soil and on hard ground like thin sheets of ice.

No remedy is yet known to neutralise its effect on vegetation, and, with the hope that this short letter may direct the attention of scientific men, I will add that I am willing to give any information in my power and supply a sample of alkali.

The first point would be to ascertain what it really is; as far as my experience goes I should call it a neutral salt, but scientific men alone can determine this, and suggest a means of neutralising its effect on vegetation.

It may prove to have a commercial value as manure.—I am, &c.,

W. R. Beauchamp.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. ciii., No. 26, December 27, 1886.

This number contains the speech of the president, M. Jurien de la Gravière, delivered at the annual public session of the Academy on Dec. 27, and an account of the various prizes awarded or offered for special researches.

*Biedermann's Central Blatt für Agrikultur Chemie.* Vol. xv., Part 8.

**Oxygen of Air in Forests.**—Prof. Erbenmeyer.—Comparative determinations made in forest air and in air from the open country show a slight preponderance of oxygen in the latter, amounting in the mean to 0·04 volume per cent, but these differences appear chiefly due to small errors in the process of examination. Air collected in calm sunny weather, immediately over the leaves, was found occasionally richer in oxygen than air from the open country. But air taken in the interior of dense thickets, between the soil and the tree-tops, was frequently rather poorer in oxygen, which may be due to the consumption of oxygen during the eremacausis of vegetable matter. Certainly there can be no at all appreciable excess of oxygen in the forests. Still, country air and especially forest air, have essential advantages as compared with town air, due to the comparative scarcity of dust, microbia, and offensive products of decomposition and putrefaction. The sanitary value of forests must rank very high.

**Nitrogen Gas in Sea-Water.**—Axel Hamberg.—From the *Journal für Praktische Chemie.*

**Carbonic Acid in Sea-Water.**—Axel Hamberg.—From the *Journal für Praktische Chemie.*

**Fixation of Nitrogen in Cultivated Soils.**—H. Joulie.—The author's experiments were made in conical glass flower-pots placed in a conservatory roofed with glass, but inclosed on the sides only with wire-gauze. An increase of nitrogen in the soil was observed in every case save one, though the arrangements excluded all considerable errors, such as may occur in experiments in an open field. According to Berthelot the fixation of atmospheric nitrogen is effected by micro-organisms, with which view the author agrees to a certain extent. In addition the plants cultivated in the soil are not without influence, and the manuring plays, beyond doubt, a capital part. The addition of marl proved most favourable, whilst the absence of potash and phosphoric acid, and above all the application of organic manures, acted unfavourably.

**Contributions to the Study of Farm-yard Manure.**—A. Audcynaud and E. Zacharewicz.—The food of the animals contained yearly 344·7 kilos. nitrogen and 188·7 potash, whilst the liquid and solid excrements contained only 158·8 nitrogen and 52·8 potash, showing a loss of 185·9 kilos, nitrogen and 135·9 potash. The skin of the horse, like that that of the sheep, exudes very considerable quantities of potash.

**Manurial Experiments with Phosphates.**—Prof. J. Fittbogen.—Ground basic slag and the precipitates obtained from it under the patents of Scheibler and Hoyermann are capable of supplying barley with the phosphoric acid necessary for a normal crop. The total of phosphoric acid required for this purpose was, however, twice as great as would have sufficed if it had been supplied as a mono- or di-calcium compound. An addition of humus improves the efficacy, both of the ground slag and of the precipitates. The precipitates do not seem to have any advantage over the ground slag.

**Utilisation of Cellulose in the Animal Organism.**—Prof. Waldemar von Knieriem.—Crude fibre must not be regarded as mere useless ballast in the food of plant-eating animals. It gives a looser texture to the contents of the bowel, and obviates the danger of obstructions. The products formed during its solution economise both fatty matters and albumenoids in the organism.

**Action of Climatic Factors upon the Growth of the Potato.**—Dr. F. C. Tschaplowitz.—This memoir does not admit of useful abstraction.

**Formation of Oxalic Acid in Plants.**—MM. Berthelot and André.—From the *Comptes Rendus.*

**Rancidity of Butter.**—E. Duclaux.—From the *Comptes Rendus.*

**Examinations of Milk in the Laboratory of the Aylesbury Dairy Company.**—Dr. P. Vieth.—If the liquid portion is removed from a partially frozen sample of milk, the ice on thawing has the composition of a watered milk. The insoluble fatty acids in pure butter range from 87·17 to 88·85, whilst in oleomargarine they reach 95·37.

**Preparation of Red Wines.**—Dr. J. Nessler.—To obtain the fullest natural colour, the fermentation should be conducted at 14° to 20°. The skins of the grapes should not be excessively comminuted. If the wine is allowed to remain in contact with the skins, stalks, &c., after the fermentation is completed a part of the colour is withdrawn from the liquid.

**Method for Determining Fusel Oil in Alcohol, especially in Brandy and Liqueurs.**—J. Traube.—The author rejects the methods now in use, and describes a

new capillarimetric process, by which fusel can be determined to about 1-50 per cent. It depends upon the fact that the rise of the aqueous solutions of organic bodies of a homologous series at the same percentage, often decreases very considerably with an increasing molecular weight of the dissolved body. Hence, especially on proper dilution, a very small proportion of fusel in brandy, &c., may be recognised by the decrease in the capillary ascent. The compounds present in fusel, the propylic and butylic alcohols, and the various aldehyds, including furfurol, reduce the ascent more than ethylic alcohol but less than amylic alcohol. The author's apparatus consists essentially of a very thin capillary tube, as narrow as possible, secured to a very fine scale, graduated in half millimetres. It terminates at its zero in two points which may be fixed exactly at the level of the liquid by means of screws. The capillary tube may easily be kept clean if it is rinsed after every experiment with water and alcohol and a current of dry air, free from dust, is drawn through it. The liquid is sucked up in the capillary two or three times and the position of the lower meniscus is read off a few hours after the liquid has come to rest. This can be done to 1-10th of a m.m., even without a lens. Liqueurs, in which the specific gravity of the distillate differs considerably from that of the original liquid, are first distilled and then diluted with water to a specific gravity corresponding to a 20 per cent (by volume) dilution of alcohol. The capillary rise, compared with that of a pure 20 per cent alcohol, shows the proportion of fusel. Differences of temperature require a very small correction.

**On Barley, Rain-drenched and Dry.**—Prof. Farsky.—Both the albumenoids and the carbohydrates undergo an extensive decomposition in barley which has been exposed to rain.

**Alleged Addition of Glycerin to the Bremen "Rose" and "Apostle" Wines.**—E. Winckelmann has recently insinuated that certain old wines in the Bremen "Council Cellar," especially the 1653 Rudesheim kept in the "Rose" vat, and the 1726 Hockheim in the "Apostle" vat, have recently received an addition of glycerin. He founds this charge on two analyses, which show that the above wines contain respectively 1 and 1·02 per cent of glycerin. E. Borgmann and J. Moritz (*Chemiker Zeitung*), two specialists, have proved, on the contrary, that the percentage of glycerin in notoriously old wines may be very high.

**Reduction of Calcium Sulphate by Certain Anærobic Ferments.**—M. Quantin.—The author observed the liberation of hydrogen sulphide due to the reduction of calcium sulphate. The process took place in cellulose, to which the microbia from swamps and mud had been added. On destroying the organisms by an addition of chloroform the reduction came to an end.

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*Moniteur Scientifique, Quesneville.*
Series 4, Vol. i., January, 1887.

**Manufacture of Safranine.**—Dr. Otto Mühlhaeuser.—A very complete account of the preparation of this colour, including a specification of the plant required for a daily yield of 36 kilos.

**Process for Determining the Number of Methoxylic Groups ($OCH_3$) contained in an Organic Derivative.**—Zeisel.—The process consists in heating the compound with hydriodic acid (prepared by means of phosphorus and of the spec. grav. 1·68) and in receiving the methyl iodide given off in an alcoholic solution of silver nitrate (two parts of the silver salt, five parts of water, and 45 c.c. of absolute alcohol). Silver iodide is formed, 1(AgI) corresponding to 1($OCH_3$).

**Researches on Papaverine.**—C. Goldschmied.—This acid, when pure, forms rhombic crystals, fusible at 147—148°, scarcely soluble in boiling water, very soluble in boiling alcohol, benzene, and acetic acid. With hot sulphuric acid it gives a violet colouration. It contains four methoxylic groups. The product resulting from the action of hydriodic acid contains four hydroxyles, and is named papaveroline.

**Patents Concerning Colouring Matters Taken at Berlin:—**

Improvements in the preparation of naphtholcarbonic acids or oxynaphthoic acids.—Dr. Von Heyden.

Preparation of benzidine-monosulphonic acid and colouring matters derived from the tetrazo-compound of this acid.—Fr. Bayer.

Preparation of soluble indulines by the reaction of aromatic diamines upon the amidoazo-compounds, oxidation of colouring matters upon the fibre.—Dahl and Co.

Preparation of the derivatives of quinizine by the action of hydrazobenzol and its homologues upon acetylacetic ether and the substitution products of this ether.—Bâle Chemical Company.

Preparation of a green-colouring matter.—Gustav Vendt.

Preparation of the mono- and disulphonic acids of tetramethyl diamido-benzophenone and tetraethyl diamido-benzophenone.—Meister, Lucius, and Brüning.

Preparation of dialkyloxylated diquinolyles and of their hydrogenated derivatives.—Bayer and Co.

Preparation of thiobenzidine, thiotolidine, and their coloured derivatives.—Dahl and Co.

Brown colouring-matters obtained by the reaction of metaphenylen-diamine or meta-toluylene-diamine upon amido-azobenzol, amido-azotoluol, amido-azoxylol, and amido-azoanisol.—Bâle Chemical Company.

Transformation of paranitrotoluene-sulphonic acid into a condensed amido-acid and into derived azo-colours.—Leonhard and Co.

Process for preparing the indol derivatives by means of the combinations formed by aromatic hydrazines with the acetones and the aldehyds treated with agents capable of removing the elements of ammonia.—Meister, Lucius, and Brüning.

Preparation of green colouring-matters by means of methylene and ethylene blues.—Meister, Lucius, and Brüning.

Preparation of diamidic and tetra-alkylic thiobenzophenones—Baden Aniline Company.

Preparation of dinitrodibenzyl.—Dr. L. F. Roser.

Preparation of a new β-naphthylamine-sulphonic acid of derived azo-colours.—Bayer and Co.

**Qualitative Analysis of Artificial Colouring Matters.**—A most valuable paper, but unfit for abstraction, and, from its bulk, incapable of reproduction in full.

**On β-Sulpho-conjugated Phthalic Acid.**—A. Ree.—From the *Journal of the Chemical Society*.

**Fortification of Wines.**—The Academy of Medicine, after a discussion extending over several sessions, has resolved that—The fortification of wines by means of pure alcohol and not beyond two degrees may be tolerated, but except under these conditions it should be absolutely prohibited. Fortification is dangerous, not only from the quantity and often from the bad quality of the alcohol added to wine, but also because it permits of subsequent watering. The so-called higher alcohols increase considerably the dangers of brandies and liqueurs. There is, therefore, reason to demand that the alcohol used in preparing these products should be absolutely pure.

**Use of an Aniline Black Varnish for the Preservation of Leather.**—L. Benoist.—This varnish, the preparation of which is not given, is said to entirely prevent leather from turning mouldy on exposure to moist air.

**The Causes of Paper Turning Yellow.**—Prof. Wiesner.—The author contends that the yellowing of paper is due to an oxidation determined by light, and especially by the more refrangible rays. This discolouration is more striking in wood-papers than in rag-papers.

Dry air is another important condition for the preservation of paper. The author thinks that in libraries the electric light is inferior to gas, on account of the large proportion of the more refrangible rays present in the former.

**Manufacture of Sodium Dichromate.**—The author uses six parts of ground chrome ore (containing 44 per cent of chromic oxide), three parts soda-ash (at 92 per cent actual carbonate), and three parts of chalk, for eight hours in the oxidising flame of a furnace capable of holding one ton of mixture. The more chromic acid is present in the finished product the more it tends to deliquesce.

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*Journal für Praktische Chemie.*
New Series, Vol. xxxiv., Part 10, 1886.

**On the Oxy-acids of Iodine.**—C. W. Blomstrand.—About few inorganic acids has so much been said as about the oxy-acids of iodine. The theory of types alone lays especial difficulties in the way of a satisfactory interpretation of these acids. As iodine itself reminds us of the metals, it may be said of periodic acid that it forms a transition to the metallic acids. This becomes evident if we compare the periodates with the salts of tungstic and molybdic acids.

**Researches from the Laboratory of Prof. A. Saytzeff, of Kasan.**—These comprise memoirs by S. Barataeff and A. Saytzeff, on the action of iodethyl and zinc upon diethylketone on the synthesis of triethel carbinol; by D. Ustinoff and A. Saytzeff, on the action of iodpropyl and zinc upon butyron; formation of dipropylcarbonol; by A. Albitzky and W. Nikolsky, on a non-volatile product of the oxidation of the hydrocarbon $C_{12}H_{20}$ obtained from allyl-dimethyl-carbinol; by D. Ustinoff, on the $\beta$-dimethyl-acrylic acid from $\beta$-dimethyl-ethylen-lactic acid obtained by the oxidation of allyl-dimethyl-carbinol; by E. Schatzky, on diallyloxalic acid and on the preparation of oxalic ether.

**Transferrers of Halogens.**—L. Meyer.—Referring to a paper on this subject by C. Willgerodt, the author states that whilst the facts laid down agree, for the most part, with those previously ascertained in the Tübingen laboratory, the inferences drawn seem in many cases premature, if not hazardous. Willgerodt is in error in assuming that the results of Page and Schenfelen are contradictory.

Part 11.

**Behaviour of Iodine with Realgar and an Arsen-iodosulphide.**—R. Schneider.—This compound, $AsI_3As_2S_3$, is a perfectly amorphous, vitreous mass, of a conchoidal fracture and a colour varying from ruby-red to reddish-brown. At ordinary temperatures it is permanent in the air. It softens at 100°, and if heated more strongly it becomes a thin liquid. It is capable of distillation, but is partially decomposed.

**Weights of Drops and their Relation to the Constants of Capillarity and on the Capillary Marginal Angle.**—J. Traube (conclusion).—The weight of drops, or the constant of capillarity, decreases with an increasing curvature of the formative surface of the drop. This decrease sets in at a certain degree of curvature, which differs for different liquids. The decrease of the weight of drops for different liquids is not proportional to the increase of curvature, but seems to be the greater the smaller the coefficient of capillarity of the liquid.

**New Apparatus for Electro-chemical Researches.**—M. von Klobulow.—This memoir requires the accompanying figures.

**Transferrers of the Halogens.**—C. Willgerodt.—The author replies to Lothar Meyer's paper in No. 10, and points out the difference between his own researches and those of Meyer and his pupils.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

**Partial Analyses of Two Samples of Sea-water, respectively taken at Scarborough and Blackpool on August 26, 1886.**—By ROWLAND WILLIAMS, F.C.S.:—

| | Grains per gallon. Scarborough. | Blackpool. |
|---|---|---|
| Total solids (dried at 220° F.) .. .. .. | 2730·55 | 2499·63 |
| Chlorine (Cl) .. .. .. .. .. .. .. | 1346·45 | 1239·52 |
| Sulphuric anhydride ($SO_3$) .. .. .. .. | 154·84 | 115·71 |
| Lime (CaO) .. .. .. .. .. .. .. | 36·42 | 46·28 |
| Magnesia (MgO) .. .. .. .. .. .. | 158·76 | 144·62 |
| Specific gravity at 60° F. .. .. .. .. | 1·0275 | 1·0244 |

## MEETINGS FOR THE WEEK.

MONDAY, 7th.—London Institution, 5.
—— Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "The Diseases of Plants," by Dr. Thudichum.
—— Society of Chemical Industry, 8. "A New Method of Elevating Liquids, especially Acids," by Mr. J. Mactear; and other papers.
—— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 8th.—Institution of Civil Engineers, 8.
—— Royal Institution, 3. "Function of Respiration," by Prof. Arthur Gamgee, F.R.S.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8. (Anniversary).
WEDNESDAY, 9th.—Society of Arts, 8. "Purity of Beer," by A. Gordon Salamon.
—— Geological, 8.
—— Microscopical, 8. (Aniversary).
—— Pharmaceutical, 8.
THURSDAY, 10th.—Royal, 4 30.
—— London Institution, 6.
—— Royal Institution, 3. "Molecular Forces," by Prof. A. W. Rücker, F.R.S.
—— Mathematical, 8.
—— Telegraph Engineers, 8.
FRIDAY, 11th.—Royal Institution, 9. "Gilded Chrysalides," by E. B. Poulton, M.A.
—— Quekett Club, 8.
—— Astronomica, 3. (Anniveisary).
—— Society of Arts, 8. "The Economical Condition of India," by Dr. George Watt, C.I.E.
SATURDAY 12th.—Royal Institution, 3. "Modern Composers of Classical Song—Rubinstein, Raff, and Grieg," by Carl Armbruster.
—— Physical, 3. Annual General Meeting. "Note on the Tenacity of Spun Glass," by E. Gibson and R. A. Gregory.

## TO CORRESPONDENTS.

*Subscriber.*—Write to the Secretary of the Institute of Chemistry, 9, Adelphi Terrace, W.C.


## PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

In the matter of Letters Patent granted to WILLIAM LLOYD WISE for "Improvements in the manufacture or production of caustic alkalies, caustic baryta, and caustic strontia (a communication), dated the 14th September, 1882, No. 4364.

NOTICE IS HEREBY GIVEN that Solvay and Company, of Brussels, Belgium (Assignees of the said Letters Patent) have applied for leave to amend the specification numbered as above.

A copy of the Specification as proposed to be amended can be inspected at the Patent Office, and particulars of the proposed amendments are set forth in the Official Journal of the Patent Office issued on the 26th January, 1887.

Any person intending to oppose the said application must leave particulars of his objections thereto (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date hereof.

Dated this 26th day of January, 1887.

(Signed) H. READER LACK,
Comptroller-General.

W. LLOYD WISE,
46, Lincoln's Inn Fields, W.C.,
Applicant's Agent.

Water-Glass, or Soluble Silicates of Soda and Potash, in large or small quantities, and either solid or in solution, at ROBERT RUMNEY'S, Ardwick Chemical Works, Manchester.

THE CHEMICAL NEWS.

Vol. LV. No. 1420.

## ON NICKEL PLATING.

By THOMAS T. P. BRUCE WARREN.

As I have not met with any reliable account of nickel plating, I am induced to put the following remarks together.

The compound used principally for the electro-deposition of nickel is a double sulphate of nickel and ammonia. The silvery appearance of the deposit depends mainly on the purity of the salt as well as the anodes. The condition of the bath, as to age, temperature, and degree of saturation, position of anodes, strength of current, and other details of manipulation, which require care, cleanliness, and experience, such as may be met with in any intelligent workman fairly acquainted with his business, are easily acquired.

In the present paper I shall deal principally with the chemical department of this subject, and shall briefly introduce, where necessary, allusion to the mechanical and electrical details connected with the process. At a future time I shall be glad to enlarge upon this part of the subject, with a view of making the article complete.

A short time ago nickel plating was nearly as expensive as silver plating. This is explained by the fact that only a few people, at least in this country, were expert in the mechanical portions of the process, and only a very few chemists gave attention to the matter; to this must be added that our text-books were fearfully deficient in information bearing on this subject.

The salt used, and also the anodes, were originally introduced into this country from America, and latterly from Germany. I am not aware of any English manufacturer who makes a speciality in the way of anodes; this is a matter on which we can hardly congratulate ourselves, as a well-known London firm some time ago supplied me with my first experimental anodes, which were in every way very superior to the German or American productions; although the price paid per pound was greater, the plates themselves were cheaper on account of their lesser thickness.

The texture of the inner portions of these foreign anodes would lead one to infer that the metallurgy of nickel was very primitive. A good homogeneous plate can be produced, still the spongy rotten plates of foreign manufacture were allowed the free run of our markets. The German plates are, in my opinion, more compact than the American. A serious fault with plates of earlier manufacture was their crumpled condition after a little use; this involved a difficulty in cleaning them when necessary. The English plates were not open to this objection; in fact, when the outer surfaces were planed away, they remained perfectly smooth and compact.

Large plates have been known to disintegrate and fall to pieces after being used for some time. A large anode surface, compared with that of the article to be plated, is of paramount importance; the tank should be sufficiently wide to take the largest article for plating, and to admit of the anodes being moved nearer to or further from the article; in this way the necessary electrical resistance can very conveniently be inserted between the anode and cathode surfaces. The elimination of hydrogen from the cathode must be avoided, or at any rate must not accumulate; moving the article being plated, whilst in the bath, taking care not to break the electrical contacts, is a good security against a streaky or foggy appearance in the deposit.

At one time a mechanical arrrangement was made, by which the cathodes were kept in motion. The addition of a little borax to the bath is a great advantage in mitigating the appearance of gas. Its behaviour is electrical rather than chemical. If the anode surface is too great, a few plates should be transferred to the cathode bars.

When an article has been nickel plated it generally presents a dull appearance, resembling frosted silver. To get over this I tried, some time ago, the use of bisulphide of carbon in the same way as used for obtaining a bright silver deposit; curiously the deposit was very dark, almost black, which could not be buffed or polished bright; but by using a very small quantity of the bisulphide mixture, the plated surfaces were so bright that the use of polishing mops or buffs could be almost dispensed with. When we consider the amount of labour required in polishing a nickel-plated article, and the impossibility of finishing off bright an undercut surface, this becomes an important addendum to the nickel-plater's list of odds and ends.

This mixture is made precisely in the same way as for bright silvering, but a great deal less is to be added to the bath, about one pint per 100 gallons; it should be well stirred in, after the day's work is done, when the bath will be in proper condition for working next day. The mixture is made by shaking together, in a glass bottle, one ounce bisulphide, and one gallon of the plating liquid; allow to stand untill excess of bisulphide has settled, and decant the clear liquid for use as required. It is better to add this by degrees than to run the risk of overdoing; if too much is added the bath is not of necessity spoiled, but it takes a great deal of working to bring it in order again.

About eight ounces of the double sulphate to each gallon of distilled or rain water, is a good proportion to use when making up a bath. There is a slight excess with this; it is a mistake to add the salt afterwards, when the bath is in good condition. The chloride and cyanide are said to give good results; I can only say that the use of either of these salts has not led to promising results in my hands.

In preparing the double sulphate, English grain nickel is decidedly the best form of metal to use. In practice old anodes are generally used.

The metal is dissolved in a mixture of nitric and dilute sulphuric acid, with the application of a gentle heat. When sufficient metal has been dissolved, and the unused nitric acid expelled, the salt may be precipitated by a strong solution sulphate of ammonia, or, if much free acid is present, carbonate of ammonia is better to use.

Tin, lead, and portion of the iron, if present, are removed by this method; the silica, carbon, and portions of copper are left behind with the undissolved fragments of metals.

The precipitated salt, after slight washing, is dissolved in water and strong solution ammonia added; a clean iron plate is immersed in the solution to remove any trace of copper. This plate must be cleaned occasionally so as to remove any reduced copper, which will impede its action. As soon as the liquid is free from copper it is left alkaline and well stirred so as to facilitate peroxidation and removal of iron, which forms a film on the bath; when this ceases the liquid is rendered neutral by addition of sulphuric acid, and filtered or decanted. The solution, when properly diluted, has sp. gr. about 1·06 at 60° F. It is best to work the bath with a weak current for a short time until the liquid yields a fine white deposit; too strong a current must be avoided.

If the copper has not been removed it will deposit on the anodes when the bath is at rest; it should then be removed by scouring.

Copper produces a reddish tinge, which is by no means unpleasant compared with the dazzling whiteness of the nickel deposit; if this is desired it is far better to use a separate bath, using anodes of suitable composition.

The want of adhesion between the deposited coating and the article need not be feared if cleanliness be attended to and the article, whilst in the bath, be not touched by the hands.

The bath should be neutral, or nearly so, slightly acid rather than alkaline. It is obvious that, as such a liquid has no detergent action on a soiled surface, scrupulous care must be taken in scouring and rinsing. Boiling alkaline solutions and a free use of powdered pumice and the scrubbing brush must on no account be neglected.

A few words on the construction of the tanks. A stout wood box, which need not be watertight, is lined with sheet lead, the joints being blown, *not soldered*. An inner casing of wood, which projects a few inches above the lead lining is necessary in order to avoid any chance of "short circuiting" or damage to the lead from the accidental falling of anodes or any article which might cut the lead. It is by no means a necessity that the lining should be such as to prevent the liquid getting to the lead.

On a future occasion I hope to supplement this paper with the analysis of the double sulphates used, and an account of the behaviour of electrolytically prepared crucibles and dishes as compared with those now in the market.

## ON ELECTRO-DISSOLUTION, AND ITS USE AS REGARDS ANALYSIS.

By H. N. WARREN, Research Analyst.

On the same principle that electro-dissolution is used for the estimation of combined carbon in steel, &c., I have lately varied the experiment by introducing, instead of steel, iron containing a certain percentage of boron, and, having connected the respective boride with the positive pole of a powerful battery, and to the negative a plate of platinum, using as a solvent dilute sulphuric acid, I observed, after the lapse of about twelve hours, the iron had entirely passed into solution, and a considerable amount of brownish precipitate had collected at the bottom of the vessel, intercepted by flakes of graphite and carbon: the precipitate, having been collected on a filter-paper, washed, and dried, on examination proved to be amorphous boron, containing graphite and other impurities, which had become chemically introduced during the preparation of the boron compound. The boron was next introduced into a small clay crucible, and intensely heated in a current of hydrogen gas, for the purpose of rendering it more dense and destroying its pyrophoric properties; and was lastly introduced into a combustion-tubing, heated to bright redness, and a stream of dry carbonic anhydride passed over it, in order to separate the carbon; finally, pure boron being obtained.

In like manner silicon-eisen, containing 9 per cent of silicon, was treated, but not giving so satisfactory a result. A small quantity only of silicon separates in the uncombined form, the greater quantity separating in the form of silica, $SiO_2$, the amorphous silicon so obtained apparently being more prone to oxidation than the boron so obtained.

Ferrous sulphide was next similarly treated, and gave, after the lapse of a few hours, a copious blackish precipitation of sulphur, and possessing properties similar to the sulphur obtained by dissolving sulphides such as cupric sulphide in dilute nitric acid, in all other respects resembling common sulphur.

Phosphides of iron, zinc, &c., were next introduced, and gave, besides carbon and other impurities, a residue containing a large percentage of phosphorus, which differed from ordinary phosphorus with respect to its insolubility in carbon disulphide, and which resembled the reaction in the case with silicon-eisen rather than that of the boron compound, insomuch that a large quantity of phosphorus had passed into solution.

A rod of impure copper, containing arsenic, iron, zinc, and other impurities, was next substituted, using hydrochloric acid as a solvent in place of sulphuric acid. In the course of a day the copper had entirely dissolved and precipitated itself on the negative electrode, the impurities remaining in solution. The copper, after having been washed, dried, and weighed, gave identical results with regard to percentage with a careful gravimetric estimation. I have lately used this method, and obtained excellent results with respect to the analysis of commercial copper, especially in the estimation of small quantities of arsenic, thus enabling the experimenter to perform his investigation on a much larger quantity than when precipitation is resorted to, at the same time avoiding the precipitated copper carrying down with it the arsenic. I have in this manner detected arsenic in commercial copper when all other methods have totally failed. I have also found the above method especially applicable with respect to the analysis of brass.

With respect to ammoniacal dissolution, of which I will briefly mention, a rod composed of an alloy of copper and silver was experimented upon, the copper becoming entirely dissolved and precipitating itself on the platinum electrode, the whole of the silver remaining suspended to the positive electrode in an arborescent form. Arsenide of zinc was similarly treated, the arsenic becoming precipitated in like manner on the platinum electrode. Various other alloys being experimented upon gave similar results.

I may also, in the last instance, mention that I have found the above methods of electro-dissolution peculiarly adapted for the preparation of unstable compounds such as stannic nitrate, potassic ferrate, ferric acetate, which are decomposed on the application of heat, and in some instances have succeeded by the following means of crystallising the resulting compound obtained.

## ANALYSES OF COMMERCIAL FERTILISERS.*

### Official Methods of the Association of Agricultural Chemists for 1886-7.

(Concluded from p. 53.)

### Determintion of Nitrogen by the Method of Kjeldahl.

*Reagents and Apparatus.*

(1) Hydrochloric acid whose absolute strength has been determined (*a*) by precipitating with silver nitrate and weighing the silver chloride; (*b*) by sodium carbonate, as described in Fresenius's "Quantitative Analysis," 2nd American edition, p. 680; and (*c*) by determining the amount neutralised by the distillate from a weighed quantity of pure ammonium chloride boiled with an excess of sodium hydrate.

(2) Standard ammonia whose strength, relative to the acid, has been accurately determined.

(3) "C. P." sulphuric acid, sp. gr. 1·83, free from nitrates and also from ammonium sulphate, which is sometimes added in the process of manufacture to destroy oxides of nitrogen.

(4) Mercuric oxide, HgO, prepared in the wet way. That prepared from mercury nitrate cannot safely be used.

(5) Potassium permanganate, tolerably finely pulverised.

(6) Granulated zinc.

(7) A solution of 40 grms. of commercial potassium sulphide in 1 litre of water.

(8) A saturated solution of sodium hydrate free from nitrates, which are sometimes added in the process of manufacture to destroy organic matter and improve the colour of the product.

(9) Solution of cochineal prepared according to Fresenius's "Quantitative Analysis, 2nd American edition, p. 679.

* From the *Proceedings* of the Third Annual Convention of the Association of Official Agricultural Chemists, at Washington, D.C., August 26 and 27, 1886. Edited by Clifford Richardson, Secretary.

(10) Burettes should be calibrated in all cases by the user.

(11) Digestion flasks of hard, moderately thick, well-annealed glass. These flasks are about 9 inches long, with a round, pear-shaped bottom, having a maximum diameter of 2½ inches, and tapering out gradually in a long neck, which is three-fourths of an inch in diameter at the narrowest part, and flared a little at the edge. The total capacity is 225 to 250 c.c.

(12) Distillation flasks of ordinary shape, 550 c.c. capacity, and fitted with a rubber stopper and a bulb tube above, to prevent the possibility of sodium hydrate being carried over mechanically during distillation. This is adjusted to the tube of the condenser by a rubber tube.

(13) A condenser. Several forms have been described, no one of which is equally convenient for all laboratories. The essential thing is that the tube which carries the steam to be condensed shall be of block tin. All kinds of glass are decomposed by steam and ammonia vapour, and will give up alkali enough to impair accuracy. (See Kreussler and Henzold, *Ber. Berichte*, xvii., 34.) The condenser in use at the laboratory of the Conn. Exp. Station, devised by Prof. Johnson, consists of a copper tank supported by a wooden frame, so that its bottom is 11 inches above the work-bench on which it stands. This tank is 16 inches high, 32 inches long, and 3 inches wide from front to back, widening above to 6 inches. It is provided with a water-supply tube which goes to the bottom, and a larger overflow pipe above. The block tin condensing tubes, whose external diameter is ⅜ths of an inch, seven in number, enter the tank through holes in the front side of it near the top, above the level of the overflow, and pass down perpendicularly through the tank and out through rubber stoppers tightly fitted into holes in the bottom. They project about 1½ inches below the bottom of the tank, and are connected by short rubber tubes with glass bulb tubes of the usual shape, which dip into glass precipitating beakers. These beakers are 6½ inches high, 3 inches in diameter below, somewhat narrower above, and of about 500 c.c. capacity. The titration can be made directly in them. The seven distillation flasks are supported on a sheet-iron shelf attached to the wooden frame that supports the tank in front of the latter. Where each flask is to stand a circular hole is cut, with three projecting lips, which support the wire gauze under the flask, and three other lips which hold the flask in place and prevent its moving laterally out of place while distillation is going on. Below this sheet-iron shelf is a metal tube carrying seven Bunsen burners, each with a stopcock like those of a gas combustion furnace. These burners are of larger diameter at the top, which prevents smoking when covered with fine gauze to prevent the flame from striking back.

(14) The stand for holding the digestion flasks consists of a pan of sheet-iron 29 inches long by 8 inches wide, on the front of which is fastened a shelf of sheet-iron as long as the pan, 5 inches wide, and 4 inches high. In this are cut six holes 1⅝ inches in diameter. At the back of the pan is a stout wire running lengthwise of the stand, 8 inches high, with a bend or depression opposite each hole in the shelf. The digestion flask rests with its lower part over a hole in the shelf, and its neck in one of the depressions in the wire frame, which holds it securely in position. Heat is supplied by low Bunsen burners below the shelf. Dr. Jenkins has used asbestos-paper under the flasks, but finds that with a little care the naked flame can be applied directly to the flask without danger.

*The Determination.*

One grm. of the substance to be analysed is brought into a digestion flask with approximately 0·7 grm. of mercuric oxide and 20 c.c. of sulphuric acid. The flask is placed on the frame above described in an inclined position, and heated below the boiling-point of the acid for from five to fifteen minutes, or until frothing has ceased. The heat is then raised till the acid boils briskly. No further attention is required till the contents of the flask has become a clear liquid, which is colourless, or at least has only a very pale straw colour. The flask is then removed from the frame, held upright, and, while still hot, potassium permanganate is dropped in carefullly and in small quantity at a time, till after shaking the liquid remains of a green or purple colour. After cooling, the contents of the flask are transferred to the distilling flask with water, and to this 25 c.c. of potassium sulphide are added, 50 c.c. of the soda solution, or sufficient to make the reaction strongly alkaline, and a few pieces of granulated zinc. The flask is at once connected with the condenser, and the contents of the flask are distilled till all ammonia has passed over into the standard acid contained in the precipitating flask previously described, and the concentrated solution can no longer be safely boiled. This operation usually requires from twenty to forty minutes. The distillate is then titrated with standard ammonia.

The use of mercuric oxide in this operation greatly shortens the time necessary for digestion, which is rarely over an hour and a half in the case of substances most difficult to oxidise, and is more commonly less than an hour. In most cases the use of potassium permanganate is quite unnecessary, but it is believed that in exceptional cases it is required for complete oxidation, and in view of the uncertainty it is always used. Potassium sulphide removes all mercury from solution, and so prevents the formation of mercuro-ammonium compounds which are not completely decomposed by soda solution. The addition of zinc gives rise to an evolution of hydrogen, and prevents violent bumping. Previous to use the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates that are present which might otherwise escape notice.

This method cannot be used for the determination of nitrogen in substances which contain nitrates or certain albumenoids.

The following references to papers in which this method is discussed may be of service:—

Kjeldahl's original paper, Fres. Zeitschr., 1883, xxii., p. 366.

Descriptions of apparatus, modifications of the process, precautions to be observed, control determinations, &c.—Maercker, Fres. Zeitschr., 1884, 223, 559. Chem. Zeitg., viii., 432. Stutzer und Reitmar, Chem. Zeitg., 1885, No. 76, from Rep. Anal. Chem., 1885, v., 232. Pfeiffer und Lehmann, Fres. Zeitschr., 1885, xxiv., 388. Kreussler, Fres. Zeitschr., 1885, xxiv., 393, 453. Landw. Versuchs. Stationen, xxxi., 269. Dafert, Fres. Zeitschr., 1885, xxiv., 454. Wilfarth, Fres. Zeitschr., 1885, xxiv., 455. Chem. Centralblatt (3 F.), xvi., 17 and 113. Rindell und Hannin, Fres. Zeitschr., 1886, xxv., 155. Czeczetka, Fres. Zeitschr., 1886, xxv., 252.

Application to determination of nitrogen in *coke and coal*.—Sigismund und Schmitz, Fres. Zeitschr., 1886, xxv., 314. In *urine*.—Petri und Lehmann, Zeitschr. für Physiolog. Chem., viii., 200. Fres. Zeitschr., 1884, xxiii., 596. Pfluger und Bohland, Pfluger's Archiv, xxxv., 454. Fres. Zeitschr., 1885, xxiv., 299. Arnold, Répertoire d. Anal. Chem., iv., 97. Hofmeister. Fres. Zeitschr., xxiv., 635. Bohland, Pfluger's Archiv, xxxvii., 423. Fres. Zeitschr., 1886, xxv., 280. In *wine*, *must*, and *yeast*.—Fres. Zeitschr., 1886, xxv., 149. In *asparagin*, *aspartic acid*, *glutamin*, *glutamic acid*, *leucin*, *tyrosin*, *allantoin*, &c.—Bosshard, Fres. Zeitschr., 1885, xxiv., 199.

Application to physiological experiments in general.—Arnold, Archiv. d. Phar. (3 R.), xxiii., 177. Fres. Zeitschr. 1886, xxv., 454.

## Determination of Nitrogen by the Ruffle Method.

*Preparation of Reagents.*

(1) A standard solution of sulphuric acid, half-normal, or 19·968 grms. $SO_3$ per litre.

(2) A standard solution of potassium hydrate, half-normal, or 27·991 grms. KOH per litre.

(3) An alcoholic solution of coralline.

(4) Hyposulphite mixture. Prepared by mixing equal parts by weight of dry slaked lime and finely-powdered crystallised sodium hyposulphite. This may be made in quantity, as it will keep dry for any length of time if kept in a well-stoppered bottle.

(5) Charcoal and sulphur mixture. This is prepared by mixing equal parts by weight of finely-powdered wood charcoal (N free) and flowers of sulphur. This must be kept in a glass-stoppered bottle. The purity of the reagents must be tested by a blank combustion.

(6) Ordinary granulated soda-lime.

*Apparatus.*

(1) Combustion tubes of hard Bohemian glass, 20 inches long and ½ inch internal diameter, drawn to a point.

(2) Three bulb 6-inch U-tubes, with glass stopcock.

(3) Aspirator.

*Preparation.*

(1) Clean and fill the U-tube with 10 c.c. of standard acid.

(2) Fit cork and glass connecting-tube. Fill the tube as follows: (1) A loosely-fitting plug of asbestos, previously ignited, and then 1 to 1½ inches of the hyposulphite mixture. (2) The weighed portion of the substance to be analysed is intimately mixed with an equal weight of the charcoal and sulphur mixture. (3) Pour on a piece of glazed paper, or porcelain mortar, a sufficient quantity of the hyposulphite mixture to fill about 10 inches of the tube; then add the substance to be analysed, as previously prepared: mix carefully and pour into the tube; shake down the contents of the tube; rinse off the paper or mortar with a small quantity of the hyposulphite mixture, and pour into the tube; then fill up with soda-lime to within 2 inches of the end of the tube. (4) Place another plug of ignited asbestos at the end of the tube, and close with a cork. (5) Hold the tube in a horizontal position, and tap on the table until there is a gas channel all along the top of the tube. Place in the furnace and make connection with the U-tube containing the acid. Aspirate and see that the apparatus is tight.

*The Combustion.*—Place the prepared combustion-tube in the furnace, letting the open end project a little so as not to burn the cork. Commence by heating the soda-lime portion until it is brought to a full red heat. Then turn up slowly jet after jet toward the other end of the tube, so that the bubbles come off two or three a second. When the whole tube is red-hot and the evolution of the gas has ceased, and the liquid in the U-tube begins to recede towards the furnace, attach the aspirator to the other limb of the U-tube, break off the end of the tube, and draw a current of air through for a few minutes. Detach the U-tube, and wash the contents into a beaker or porcelain basin; add a few drops of the coralline solution, and titrate.*

### Determination of Nitrogen by the Soda-Lime Method.

Select a tube of hard glass 14 to 16 inches long, draw one end of it to a fine point, and to the other end fit a cork, through which is passed a tube bent at right angles, the other end of which passes through a cork closing tightly one arm of a 6-inch three-bulbed U-tube with glass stopcock. Into the combustion-tube first slip a loosely-fitting plug of asbestos, previously ignited, and then 1½ to 2 inches of soda-lime. Weigh out from 0·7 to 2·8 grms. of the substance to be analysed, and mix it on a piece of glazed paper or porcelain mortar with some finely-pulverised soda-lime, and introduce the mixture into the combustion-tube. The paper or mortar is then rinsed out with a small quantity of soda-lime and poured into the tube. The tube is then filled up to within 1 to 2 inches of the open end with granulated soda-lime, then fill up with a plug of ignited asbestos. A free passage is formed for the evolved gases by holding the tube in a horizontal position and tapping gently on the table. Introduce the prepared combustion-tube into the furnace, letting the open end project a little so as not to burn the cork, supporting the U-tube by a clamp. The tube is then gradually heated, commencing at the fore part, nearest the cork, and progressing slowly towards the tail. The combustion should be conducted so as to obtain a steady and uninterrupted flow of gas. When properly carried out the acid in the U-tube is never coloured. When the acid begins to recede attach the aspirator to the other limb of the U-tube, and start it slowly, then break off the point of the combustion-tube and draw a current of air through the apparatus for a few minutes, in order to sweep all the ammonia into the acid.

Detach the U-tube and wash the contents into a beaker or porcelain basin, add a few drops of an alcoholic solution of coralline and titrate.

The standard acid, alkali, and indicator to be the same as that used in the Ruffle method.

* Cochineal may be found a better indicator, as the $H_2S$ evolved in the combustion affects coralline.—(C. R.)

## PROPOSED AUSTRALASIAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

On Wednesday, November 10th, 1886, a preliminary meeting of the delegates appointed by the principal Australasian societies was held, Mr. H. C. Russell, F.R.S., being in the chair. The object of the meeting was to consider the proposal for forming an Australasian Association for the Advancement of Science. The proposal has met with considerable support from nearly all the Australian societies, Prof. Liversidge, F.R.S., of the Royal Society of New South Wales, being a very energetic promoter of the scheme.

At the meeting referred to above it was decided to found the Society on the same lines as the British Association for the Advancement of Science, and a resolution was passed adopting the Rules as printed of the last-named Association. The objects of this new Association are in every way similar to those of the older one in England, even to the excursions to places of interest in the neighbourhood of the towns where the meetings are to be held.

The first and inaugural meeting is proposed to be held at Sydney, in the year 1888, that year being the hundredth anniversary of the founding of the colony of New South Wales.

The Committee meetings for making the preliminary arrangements are held at the House of the Royal Society of New South Wales, Elizabeth Street, Sydney. This Society is certainly doing its best for the advancement of Science in the Colonies, and with that object they have offered medals and money prizes for original researches on the following subjects:—

Series VI.—To be sent in not later than 1st May, 1887.

No. 20. On the Silver Ore Deposits of New South Wales. The Society's medal and £25.

21. Origin and Mode of Occurrence of Gold-bearing Veins and of the associated Minerals. The Society's medal and £25.

22. Influence of the Australian Climate in producing Modifications of Diseases. The Society's medal and £25.

23. On the Infusoria peculiar to Australia. The Society's medal and £25.

Series VII.—To be sent in not later than 1st May, 1888.

No. 24. Anatomy and Life History of the Echidna and Platypus. The Society's medal and £25.

25. Anatomy and Life History of Mollusca peculiar to Australia. The Society's medal and £25.

26. The Chemical Composition of the Products from the so-called Kerosene Shale of New South Wales. The Society's medal and £25.

SERIES VIII.—To be sent in not later than 1st May, 1889.

No. 27. On the Chemistry of the Australian Gums and Resins. The Society's medal and £25.

28. On the Aborigines of Australia. The Society's medal and £25.

29. On the Iron Ore Deposits of New South Wales. The Society's medal and £25.

30. List of the Marine Fauna of Port Jackson, with Descriptive Notes as to Habits, Distribution, &c. The Society's medal and £25.

The competition is in no way confined to Members of the Society, nor to residents in Australia, but is open to all without any restriction whatever, excepting that a prize will not be awarded to a Member of the Council for the time being; neither will an award be made for a mere compilation, however meritorious in its way; the communication to be successful must be either wholly or in part the result of original observation or research on the part of the contributor.

The Society is fully sensible that the money value of the prize will not repay an investigator for the expenditure of his time and labour, but it is hoped that the honour will be regarded as a sufficient inducement and reward.

The successful papers will be published in the Society's annual volume. Fifty reprint copies will be furnished to the author free of expense.

Competitors are requested to write upon foolscap paper, on one side only. A motto must be used instead of the writer's name, and each paper must be accompanied by a sealed envelope bearing the motto outside and containing the writer's name and address inside.

All communications to be addressed to the Honorary Secretaries, who are Messrs. A. Liversidge and F. B. Kyngdon.

Such efforts as these are sure to command success, and we are happy to see that the scientific future of one of our finest Colonies is assured.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, February 3rd, 1887.*

Dr. HUGO MÜLLER, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Cecil Howard Cribb, 38, Soho Square; Joseph Frank Geisler, Mercantile Exchange Buildings, Hudson and Harrison Streets, New York; Thomas Albert Hedley, 41, St. Jean Baptiste Street, Montreal; Joseph William O'Connor, Aberaeron Place, N.W.; Gerald Tattersal Moody, 229, Rye Hill, S.E.

The following were elected Fellows of the Society:—Messrs. William Henry Coates, Thomas Cooksey, Arthur Henry Downes, M.D., Hamilton Emmons, George Arthur Goyder, E. Hori, Hubert McKeow, J. F. McArthur, David Henry Nagel, Thomas Burden Reay, Charles E. Sohn, jun., Lionel W. Stansell, James Pim Strangman, D. A. Sutherland, Jokichi Takaminé.

The following papers were read:—

5. "*The Absorption of Gases by Carbon.*" By CHARLES J. BAKER.

A series of experiments are described in which carbon in the form of animal charcoal, previously heated *in vacuo*, was saturated with oxygen, both dry and moist, at a low temperature; the carbon thus treated, enclosed in a vacuous tube, was then heated for some time at 100°, and finally the absorbed gas was extracted and analysed.

Using moist oxygen, it was found that no gas was given off at 12° from the carbon which had been exposed for one hour at −15° in such an atmosphere; on heating the carbon thus treated at 100° during seven days, and then exhausting at this temperature, it gave about seven times its volume of gas, consisting of carbon dioxide. No carbon dioxide was produced on digesting carbon and water vapour for a similar period and then exhausting.

Using dry oxygen and proceeding similarly, no gas was given off from the charcoal at 100°; however, on raising the temperature to about 450°, gas was expelled, consisting mainly of carbon monoxide mixed with carbon dioxide. Dried carbon was then charged with dried carbon dioxide, and the gas was extracted by heating at about 450° as before; it consisted of carbon monoxide and dioxide, the proportion of the former being less the more carefully the carbon was dried. The author therefore concludes that the more carefully moisture is excluded the less does the carbon burn in the carbon dioxide which it absorbs; and, further, that carbon is burned directly to carbon monoxide by absorbed oxygen.

### DISCUSSION.

Mr. F. J. M. PAGE asked whether the author had ascertained if the same carbon could be used repeatedly; that is to say, was it possible to burn away the whole of the carbon, or was the action confined to the surface?

Prof. ODLING, who had communicated the paper, said this had not been ascertained; he thought, however, it was probable that the carbon would become less and less absorptive, but that the action would continue in proportion as absorption took place.

6. "*An Explanation of the Laws which govern Substitution in the case of Benzenoid Compounds.*" By HENRY E. ARMSTRONG.

Certain mono-derivatives of benzene, especially those containing a hydrocarbon radicle, one of the halogens, hydroxyl or amidogen, yield a mixture of the para- and ortho-di-derivatives in proportions which vary both according to the nature of the compound dealt with and of the reagent, and the conditions under which the change is effected; and if produced at all, the meta-derivative is formed in but a small proportion. If, however, the radicle present in the mono-derivative be $NO_2$, COH, $CO_2H$, $SO_3H$, the meta-di-derivative appears invariably to be the chief product. Hitherto no explanation of this difference in the behaviour of the two series of mono-derivatives has even been suggested.

In seeking to arrive at an explanation it is necessary to form a clear conception of the manner in which "substitution" is effected. The author is of opinion that in the first instance an additive compound is formed, and he points out that Kekulé has long since insisted in the plainest terms on this interpretation of changes of so-called double decomposition.

He is inclined to believe that the tendency of negative to attract and combine with negative elements—to which he has of late frequently directed attention—is the effective cause, and that the additive compound is formed from those mono-derivatives which obey the "para-ortho law" by the fixation of the reacting molecule upon the carbon-atom which carries the radicle: separation of water or halogen hydride ensuing thereon, the radicle of the reacting molecule assumes the place either of an ortho- or of a para-hydrogen atom. It is easy to understand the formation of the ortho-di-derivative, as the hydrogen-atom displaced is associated with a carbon-atom contiguous to that to which the reacting molecule attaches itself. The formation of the para-compound is attributed by the author to the tendency towards symmetry, so frequently evidenced in cases of isomeric change and in other ways by benzenoid compounds, and not to the existence of any direct connexion between carbon-atoms relatively in the para-position. The formation of meta-derivatives is be-

lieved by the author to result from the addition of the reacting molecule, not to the carbon-atom of the benzene ring, but *to the radicle* which in the mono-derivative is attached to one of the carbon-atoms of the ring; he is, however, of opinion that in order to explain why the additive compound thus constituted yields a meta-di-derivative, it will be necessary to obtain further information regarding the "dynamics" of such changes.

Discussion.

Professor Odling observed that any attempt to solve the problem of the action of the commonly employed reagents, chlorine or bromine, nitric acid and sulphuric acid on one set of phenic mono-derivatives to produce under ordinary conditions mainly para-di-derivatives, and on another set of phenic mono-derivatives to produce mainly meta-di-derivatives, was entitled to a thoughtful and grateful consideration. But in his opinion a distinction should be drawn between the abstract cause of the result—as when Prof. Armstrong attributed the habitual preferential formation of para-derivatives to the existence of a tendency to the formation of symmetric compounds, and the mechanism leading to the result—as when he represented the formation of ortho-derivatives as being an almost necessary consequence of the particular process by which he conceived the substitution to be effected. The former suggestion did not appear to help the matter forward very much; but the latter suggestion was at any rate in the nature of a real explanation; though, for himself, he was not prepared to admit the general principle; that the previous combination of reagents was an invariable and determining condition of their reaction. Under exposure to bright daylight, a mixture of equal volumes of chlorine and marsh-gas, for instance, reacted even with violence; and, in his opinion, while the evidence as to the fact of their previous combination was of the smallest, the evidence as to the previous combination being the determining condition of the reaction was none at all. Admitting, however, that in the case of phenic reactions a previous combination took place in the particular manner so ingeniously conceived by Professor Armstrong as favouring the production of ortho-compounds, the general question, exemplified in the special case of the nitro-bromo-derivatives, for instance, why, starting from the mono-bromo-derivative we should get mainly a para-di-derivative instead of an ortho-di-derivative, and why, starting from the mono-nitro-derivative we should get mainly a meta-di-derivative rather than either a para- or an ortho-di-derivative, still remained a problem, and one of very great interest, towards the solution of which Professor Armstrong had, at any rate, made a serious advance. It was clear that the nature of the product depended a good deal on the conditions of, and modes of effecting, the reaction; but having regard to the usual modes of experimenting, he was accustomed to point out that where the pre-existing radicle was one of the typical radicles formulated as Cl, OH, $NH_2$, and $CH_3$, respectively, or some closely related radicle, the tendency was to the formation of 1—4 di-derivatives; and that where the pre-existing radicle was one of the acidic radicles formulated as $NO_2$, $SO_3H$, and $CO_2H$, or some allied radicle, the tendency was to the production of 1—3 di-derivatives. Having regard to the want of absolute concordance even in the writings of the present day, and to the extreme confusion in the writings of the last twenty years, as to the attribution of the prefixes para-, ortho-, and meta-, he preferred to speak of the different sets of compounds as 1—4, and 1—2, and 1—3 derivatives respectively. At the same time the expression of the primary 1, in each case, was for the most part superfluous, and might be omitted with advantage; only, to avoid confusing the other numerals with multiples, it was preferable to denote them by means of the small Roman or italic figures used by doctors when writing their prescriptions, instead of by the usual Arabic figures. Thus while speaking of the two liquid dibromobenzenes, or as he preferred to call them dibromo-phenoenes, as one-two and one-three dibromophenoene respectively, he was accustomed to write and formulate them as ij-dibromo-phenoene or ij-$C_6H_4Br_2$, and iij-dibromo-phenoene or iij-$C_6H_4Br_2$ respectively, the so-printed names and formulæ being much shorter and clearer than those usually employed. These expressions, moreover, stand in direct relation to the facts that ij-dibromo-phenoene gives origin to two tribromo-derivatives, and that iij-dibromo-phenoene gives origin to three tribromo-derivatives. As regards the expression of the 1—4 or crystalline dibromo-phenoene, he was accustomed to write and formulate it as jv-dibromo-phenoene, or jv-$C_6H_4Br_2$; but it might be very well expressed as j-dibromo-phenoene or j-$C_6H_4Br_2$, which would associate it with the fact of its giving origin to one tribromo-phenoene only.

Mr. Groves referred to the absorption of chlorine in large quantity by chloroform and carbon tetrachloride, and thought that facts such as these ought to be taken into account. He did not think that the tendency to form symmetrical di-derivatives was so universal as suggested by the author: the formation of resorcinol from benzene-*para*disulphonic acid was a case in point.

Dr. W. H. Perkin, Jun., thought that the production from hydrazo-benzene, not only of benzidine but also of an isomer, was evidence against Dr. Armstrong's view as to the manner in which para-compounds were formed.

Dr. Armstrong, replying to Prof. Odling's objection that the para-derivative was the chief product, and not the ortho- as should be the case according to his (Dr. Armstrong's) explanation of the manner in which substitution was effected, said that this was by no means always the case: in a recent investigation of the chlorotoluenes, for example, it had been shown that about twice as much ortho- as para-dichlorotoluene was formed. The proportions in which para- and ortho-derivatives were formed appeared, however, to vary greatly, and to depend very much on the conditions obtaining at the time of change. He was of opinion that the behaviour of the paraffins afforded the strongest evidence in support of his view that addition preceded substitution: the affinity of the carbon-atoms being all but satisfied, especially in the lowest terms, substitution was effected but slowly in consequence of the small extent to which the chlorine was able to combine with the paraffin; and it was most important to observe that when chlorine had once become introduced, the introduction of other atoms could be effected more and more readily—the chlorine already introduced rendering the molecule more ready to combine with chlorine. Mr. Groves's reference to the solubility of chlorine in chloroform and carbon tetrachloride was most apposite. The behaviour of hydrazobenzene appeared to him to be perfectly in harmony with his views, the isomer formed along with benzidine being the ortho-compound. Cases such as were referred to by Mr. Groves were probably not simple isomeric changes, but involved the successive occurrence of several distinct changes.

7. "*Some Derivatives of Tetramethylene.*" By G. H Calman and Dr. W. H. Perkin, Jun.

On heating calcium tetramethylenemonocarboxylate with lime, a gas and an oil are produced, two-thirds of the former consisting of ethylene, and the remaining third being a mixture of hydrogen, methane, and carbonic oxide.

The oil contains two new ketones, namely, ditetramethylene ketone—

$$CH_2\begin{Bmatrix}CH_2\\CH_2\end{Bmatrix}CH\cdot CO\cdot CH\begin{Bmatrix}CH_2\\CH_2\end{Bmatrix}CH_2.$$ B.-p. 204—205°;

and methyltetramethylene ketone or acetyl-tetramethylene—

$$CH_3\cdot CO\,CH\begin{Bmatrix}CH_2\\CH_2\end{Bmatrix}CH_2.$$ B.-p. 137—138°.

Tetramethylene aldehyde has also been prepared by heating calcium tetramethylenemonocarboxylate with calcium formate; it boils at 115—117°.

8. "*Derivatives of Pentamethylene.*" By Dr. W. H. Perkin, Jun.

The sodium-derivative of ethyl malonate is converted by the action of trimethylene bromide into ethylic tetramethylenedicarboxylate and ethylpentane-$\omega_2$ $\omega_2$-tetracarboxylate,—

$$(COOEt)_2{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOEt)_2.$$

On hydrolysis this latter yields the tetracarboxylic acid, which on heating to 200° is converted into $\alpha$-pimelic acid and carbonic anhydride.

If ethylic pentanetetracarboxylate be treated with sodic ethylate, a disodium compound,—

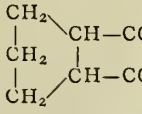
$$(COOEt)CNa{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CNa{\cdot}(COOEt)_2,$$

is formed: ethylic pentamethylenetetracarboxylate,—

$$(COOEt)_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(COOEt)_2,$$

is obtained by treating this disodium-derivative with bromine.

On hydrolysis this salt yields the tetracarboxylic acid, which on heating to 200° gives off 2 molecules of carbonic anhydride, being converted into pentamethylenedicarboxylic acid,—



a crystalline body melting at 160°.

Ethylic pentamethylenedicarboxylate is a disagreeably smelling oil, boiling at 249—252°.

Pentamethylenedicarboxlic anhydride melts at 64—67°.

Discussion.

Dr. A. K. Miller asked, Had Dr. Perkin made any attempts to prepare hexamethylene rings? Reactions which would furnish compounds so constituted might easily be suggested; and their production would afford considerable support to the arguments adduced in favour of the view that those now described were tetra- and pentamethylene ring-compounds.

Dr. Armstrong remarked on the peculiarly interesting and valuable character of Dr. Perkin's work. In his paper on tetramethylene compounds Dr. Perkin had most clearly established the difference between what he called tetramethylene compounds and the *known* isomeric allyl-derivatives which it was conceivable might be formed in reactions such as were described; but it did not follow from this that the bodies in question were tetramethylene compounds: we were admittedly dealing with bodies of a novel type, and it was therefore necessary to be very cautious in applying knowledge gained by study of their physical properties, as we were unacquainted with the properties of any comparable series of compounds. Great differences were to be noted between maleic and fumaric acids, and between citra-, ita-, and mesaconic acids, which could not at present be satisfactorily explained in terms of our conventional symbols; in like manner, it was conceivable that open-chain compounds might exist having properties very different from those of the known allyl-derivatives.

Dr. Perkin, Sen., said that in their physical properties the compounds discovered by his son were altogether peculiar: they behaved nearly as saturated bodies, and therefore the only way at present of representing them was to employ closed-chain formulæ. The maleic compounds behaved as unsaturated bodies, and the fumaric compounds were still further removed from saturated compounds. The properties of the tetramethylene compounds were in no sense akin to those of the maleic-fumaric, or citra-ita-mesaconic series.

Dr. Perkin, Jun., said that in the paper referred to he had only sought to prove that allylacetic and allylmalonic acids were different from what he had termed tetramethylene mono- and dicarboxylic acids; the latter might have some quite different formulæ to those which he had proposed, but they could not be regarded as parallel compounds to the fumaric or itaconic acids.

Dr. Armstrong added that it must not be forgotten that trimethylene, $CH_2{\cdot}CH_2{\cdot}CH_2$, although unsaturated, behaves practically as a saturated compound.

9. "*The Decomposition of Potassium Chlorate and Perchlorate by Heat.*" By Percy F. Frankland, Ph.D., B.Sc., A.R.S.M., and John Dingwall.

The authors have re-investigated the points in the decomposition of these bodies which were raised by Teed (*Proc. Chem. Soc.*, Nos. 12 and 16, 1885-86).

In the first series of experiments potassium chlorate was partially decomposed by heating in a tube over a naked flame. The results are summarised in Table I.

In further experiments the potassium chlorate was decomposed at a temperature below that at which potassium perchlorate suffers change, by heating it in the vapour of boiling sulphur. (See Table II.)

It appears, therefore, that when potassium chlorate is partially decomposed by heat, the decomposition may be expressed by equations of the type—

$$8KClO_3 = 2O_2 + 5ClO_4 + 3KCl,$$

and that the more complete the decomposition the more does it approximate to that indicated by the equation $2KClO_3 = KClO_4 + KCl + O_2$.

The authors have fully established the formation of potassium chlorate in the first stages of the decomposition of potassium perchlorate. This reaction is of interest as forming an exception to Berthelot's law of maximum work, the well-known formation of potassium perchlorate from potassium chlorate being a reversible reaction.

In a first series of experiments with perchlorate, the potassium chlorate was determined by means of the zinc-copper couple method. Finding, however, that the sample had a very slight action on perchlorates, a second series of experiments were made, in which the chlorate formed was determined by evaporation with chlorhydric acid; the results entirely substantiate those of the first series, and are as shown in Table III.

10. "*The Action of Chlorine on Methyl Thiocyanate.*" By Dr. J. William James, University College, Cardiff.

The author describes the result of the action of chlorine on methyl thiocyanate, a reaction first studied by Cahours, and afterwards by Riche.

On passing dry chlorine into methyl thiocyanate at the ordinary temperature, to complete saturation, the reaction being completed in sunlight, methyl thiocyanate is decomposed into *cyanuric chloride*, *thiocarbonyl chloride* ($CSCl_2$), and the *tetrachloride*, $CSCl_4$. The latter is identical with the perchlormethylmercaptan of Rathke, obtained by the action of chlorine on carbon disulphide in presence of iodine. The chief reaction which takes place is—

$$3CH_3SCN + 11Cl_2 = C_3N_3Cl_3 + 2CSCl_4 + CSCl_2 + 9HCl.$$

Cahours studied the reactions in a qualitative manner only; and Riche did not show the presence of ether thiocarbonyl chloride or tetrachloride, and, moreover, obtained a body of the formula $C_2SCl_6$, which, as is shown, must have been a mixture of $CSCl_4$ and $C_3N_3Cl_3$.

The author has further established, that when chlorine is passed into thiocarbonyl chloride, it is completely absorbed, forming thiocarbonyl tetrachloride; and that by the prolonged action of the gas this latter substance is decomposed into carbon tetrachloride and sulphur dichloride.

The well-known fact that carbon disulphide is converted by chlorine into these two bodies seems now to be the result of a series of reactions, viz.: (1) $CS_2 + 2Cl_2 = CSCl_2 + SCl_2$; (2) $CSCl_2 + Cl_2 = CSCl_4$; (3) $CSCl_4 + Cl_2 = CCl_4 + SCl_2$.

——

At the next meeting, on February 17th, the following papers will be read:—

TABLE I.

| Percentage of oxygen evolved on weight of $KClO_3$ taken. | On $KClO_3$ actually decomposed. Percentage of oxygen evolved. | KCl formed (per cent.) | $KClO_4$ formed (per cent.) | Proportion of oxygen evolved to 74·57 parts of KCl formed. |
|---|---|---|---|---|
| No. 1. 2·66 | 6·30 | 22·48 | 71·22 | 20·87 |
| No. 2. 5·19 | 6·27 | 22·43 | 71·30 | 20·84 |
| No. 3. 6·47 | 7·09 | 23·68 | 69·23 | 22·32 |
| Equation— | | | | |
| $10KClO_3 = 6KClO_4 + 4KCl + 3O_2$ requires | 7·83 | 24·34 | 67·83 | 24·00 |
| $8KClO_3 = 5KClO_4 + 3KCl + 2O_2$ requires | 6·53 | 22·81 | 70·66 | 21·33 |
| $2KClO_3 = KClO_4 + KCl + O_2$ requires | 13·05 | 30·42 | 56·53 | 32·00 |

TABLE II.

| Percentage of oxygen evolved on weight of $KClO_3$ taken. | On $KClO_3$ actually decomposed. Percentage of oxygen evolved. | KCl formed (per cent.) | $KClO_4$ formed (per cent.) | Proportion of oxygen evolved to 74·57 parts of KCl formed. |
|---|---|---|---|---|
| No. 1. 6·80 | 8·14 | 25·44 | 66·42 | 23·88 |
| No. 2. 6·78 | 8·76 | 26·03 | 65·21 | 25·10 |
| No. 3. ($KClO_3$ mixed with powdered glass) 14·30 | 15·34 | 33·55 | 51·11 | 34·10 |

TABLE III.

| Percentage of oxygen evolved on weight of $KClO_4$ taken. | On $KClO_4$ decomposed. Oxygen evolved (per cent). | KCl formed (per cent). | $KClO_3$ formed (per cent). | Oxygen evolved to 74·57 parts of KCl formed. |
|---|---|---|---|---|
| No. 1. 6·34 | 36·54 | 38·70 | 24·76 | 70·41 |
| No. 2. 7·80 | 36·63 | 38·79 | 24·58 | 70·42 |
| No. 3. 24·05 | 43·60 | 49·21 | 7·19 | 66·06 |
| The equation— | | | | |
| $7KClO_4 - 2KClO_3 + 5KCl + 11O_2$ requires | 36·29 | 38·44 | 25·27 | 70·40 |

"The Influence of Temperature on the Heat of Dissolution of Salts," by S. U. Pickering.

"Researches on the Laws of Substitution in the Naphthalene Series" (Part III.), by Dr. Armstrong.

## CORRESPONDENCE.

### ON THE COMPOSITION OF HYDRATED SALTS.

*To the Editor of the Chemical News.*

SIR,—I have done my utmost to simplify the question of hydrates, but Mr. Pickering cannot make up his mind to face it. A fortnight ago he used the words "*galli cantus*," to-day "Arcadian simplicity."

I cannot continue any longer a discussion on a subject of such very great simplicity. I hope that English chemists will not lose the chief point, viz., the determination not to desiccate properly, 1st, the alum under examination, by means of a large mass of very dry alum. I repeat that the alum remains perfectly transparent up to the last moment (constant weight) with this method of desiccation, and that, if it is then put under a shade with sulphuric acid, one hour afterwards the crystals have a whitish appearance at the angles: this is the commencement of dehydration. 2nd. The same must be done in the case of sulphate of magnesia.—I am, &c.,

E. MAUMENÉ.

### COHESION AND SUBMERSION FIGURES: THE NATURE OF SOLUTION.

*To the Editor of the Chemical News.*

SIR,—The reference to me in the CHEMICAL NEWS (vol. lv., p. 1) calls for a few remarks on my part. As far as I was aware at the time of writing, each of my notes on "Cohesion and Cohesion Figures" (CHEMICAL NEWS, vol. liv., p. 58) contained at least one original idea. I do not remember to have read of such a thing as a solidified vortex ring before, or of a comparison such as I make of the life-history of liquid and gaseous vortex rings with a view to showing their possible identity. I drew this analogy some years ago in the first issue of *Science for All* (vol. iv., p. 200), where I refer to Mr. Tomlinson, who is acknowledged to be the British authority on this subject, as his paper in the CHEMICAL NEWS (vol. lv., p. 1) well shows.

Nor do I remember to have before seen laid down the connection between cohesion and solution. The notes 1 and 2 (CHEMICAL NEWS, vol. liv., p. 58), on "A Law of Solubility" and "Its Connection with Mendeleeff's Periodic Law" were written by me before any advertisement had appeared of the proposed 1886 B.A. "Discussion of the Nature of Solution." Three weeks after their publication Dr. Tilden's letter appeared in your columns, indicating the general nature of the subjects upon which he intended to offer remarks, and one of the headings was "Is there any general connection between solubility and atomic weight in a series of compounds in which only one constant varies?" (CHEMICAL NEWS, vol. liv., p. 95). This was the subject of my note 2, where I show that in one natural series of compounds, the chlorides of Mendeleeff's Group I., as the atomic weight of the variable decreases the solubility of the compound in water increases; and one may imagine, as a working hypothesis, that if water had had a greater molecular weight than the heaviest of this series the relation would have been a direct instead of an inverse one. In the following September the relation of kinship to solubility was dwelt upon at the B.A. meeting, according to the reports in your columns. Dr. Tilden pointed out that the salts containing water of crystallisation, as resembling water, are for the most part soluble in water (CHEMICAL NEWS, vol. liv., p. 183), and Dr. Armstrong gave many cases of like

dissolving like (Chemical News, vol. liv., p. 218) which are illustrative of the law I formulated in my prior note 1.

I am aware that coincidences of this kind are common (*vide* Chemical News, vol. liv., p. 239), and I request leave to point them out in the present instance because my terse notes give no idea of the time and thought I have expended on the subject since 1877, and I would not have them ignored because of their terseness.—I am, &c.,

William Ackroyd.

Borough Laboratory, Halifax,
January 29, 1887.

## ALKALI—CALIFORNIA.

*To the Editor of the Chemical News.*

Sir,—Mr. Beauchamp has brought to me two or three samples of the efflorescence from the soil in California. It is sodium sulphate, or thenardite, more or less pure. I fear it is of very little value at present.—I am, &c.,

John Attfield.

17, Bloomsbury Square,
February 5, 1887.

## VAPOUR DENSITY.

*To the Editor of the Chemical News.*

Sir,—Victor Meyer's method of determining vapour densities is recommended for its simplicity, accuracy, and suitability for liquids of both high and low boiling-points. But in attempting to make determinations of the vapour densities of volatile bodies, as chloroform, I find it impossible to prevent the water of the trough from rushing into the tube during vaporisation of the body experimented upon.

Would someone of experience indicate the cause, and therefore the prevention, of this source of error and annoyance?—I am, &c.,

J. W. S.

New Mills, February 6, 1887.

## PYROMETRIC MEASUREMENTS OF HIGH TEMPERATURES.

*To the Editor of the Chemical News.*

Sir,—Referring to MM. Ch. Lauth and G. Vogt's indicators of temperature, "Fusible Watches" (Chemical News, vol. lv., p. 47), I used similar indicators twenty-eight years ago, to determine temperatures when baking ultramarine mixtures. My indicators were composed of litharge, pipeclay, lime, and borax, finely ground; the mixture after moistening with water being formed into small cones, and, after drying, partially baked. I found that they gave most reliable results.—I am, &c.

M. A. Gage.

Rhuddlan, Flintshire, Feb. 8, 1887.

## THE ANALYSIS OF OPIUM.

*To the Editor of the Chemical News.*

Sir,—Mr. Stillwell's method for the estimation of morphia in opium, as described in the Chemical News (vol. lv., pp. 41 and 54), is very similar in most respects to one which has been employed in my laboratory for the same purpose during the past year.

The essential points of difference are—(1), the degree of concentration of the opium solution—Mr. Stillwell evaporating the fluid to a somewhat smaller bulk than I consider necessary; (2), the strength of the ammonia solution employed for precipitating the morphia—Mr. Stillwell using ammonia of 0·960 sp. gr., whereas I use a *smaller quantity* of strong ammonia, sp. gr. 0·880; and, (3), instead of purifying the weighed morphia by means of hot alcohol, I check my results by titrating the precipitate with decinormal sulphuric acid. The titration with acid generally gives figures from 0·10 to 0·25 per cent lower than those obtained by simply weighing the morphia.

I can highly recommend Mr. Stilwell's method, as it may be relied upon to extract *all* the morphia present, which most other processes fail to do; and the morphia obtained is also much purer than that yielded by any other with which I am acquainted.—I am, &c.,

Rowland Williams.

9, Albert Square, Manchester, Feb. 7, 1887.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Journal de Pharmacie et de Chemie.*
Fifth Series, Vol. xiv., No. 12, December 15, 1886.

**On an Epidemic of Micrococcus prodigiosus.**—M. Grimbert.—The author had the opportunity of examining some cooked meat covered with carmine spots, which smeared off on touching. They were due to a microbian vegetation capable of being planted in other organic matter, *e.g.*, boiled potatoes. The colouring-matter is very soluble in alcohol, ether, chloroform, and carbon disulphide. The spectroscopic examination of the alcoholic solution showed a well-marked absorption-band between the rays D and E, and then a feebler band near the ray *b*, and a gradual extinction of the other colours up to the violet.

**Areometric Determination of the Alcohol in Wines. Vinodensimeter.**—A. Bouriez.—Already noticed.

Vol. xv., No. 1, January, 1887.

**Assay and Analysis of Officinal Quinine Sulphate.**—E. Jungfleisch.—In this first memoir the author criticises the process laid down in the French codex, and states that its sensitiveness is so much the greater as the sample is dissolved at a higher temperature. He recommends 100°. He does not approve of the optical test unless the absolute purity of the quinine used in medicine is to be insisted upon.

**Decomposition of Oiled Silk and Oil Paintings.**—M. Balland.—Already noticed.

**Preparation and Examination of Acetanilide.**—M. Yvon.—This paper has merely a pharmaceutical interest.

**Internal Hygiene of Houses illuminated by the Electric Light.**—Dr. Sambuc.—The author refers to glow-lamps worked by means of the Grevet battery. To prevent mischief he recommends that cells of porcelain or stoneware should be used for the batteries, that the sulphuric acid should be diluted and let cool before immersing the zinc, that the depolarising agent should not be mixed with the exciting liquid, that the zinc should be of good quality, free from arsenic, and well amalgamated, and that the battery should be fixed in a garden, a court, or a cellar.

**Sensitiveness of Some Reagents for Albumen.**—M. Simon.—The most sensitive reagent is that of Méhu, a mixture of 1 part crystalline phenic acid with one part acetic acid and 2 parts water.

**On the Alleged Soluble Starch.**—J. Kraus.—The substance found in the epidermis of *Ornithogala* and *Gagea*, although it is coloured blue by iodised water, is not a starch, and should rank near the tannins. The reaction with iodine is not surprising, since Giessmayer has shown that solution of tannin in a slightly alkaline liquid gives a bright red colour with a weak solution of iodine.

Nasse has shown that tannin, gallic, and pyrogallic acids, liberated in presence of neutral or acid salts, is turned a reddish purple by iodine.

**Chemical and Pysiological Study of Methylal.**—E. Personali.—Methylal is a novel hypnotic agent of the composition $C_3H_8O_2$.

**Distinctions between the Colcurations of Urine by Chrysophanic Acid and by Santonine.**—M. Hoppe-Seyler.—These colourations may be distinguished by adding to the urine caustic soda, and then agitating with amylic alcohol. If the colouration is due to santonine the colouring-matter passes almost entirely into the solvent, and the urine is decolourised. If it is derived from chrysophanic acid the amylic alcohol takes up mere traces and the urine remains red. But if the urine is acidulated, the chrysophanic acid may be removed by amylic alcohol, and if the solvent is then shaken up with ammonia the aqueous stratum is reddened. Under the same circumstances the colouring-matter of santonine is not removed. The absorption spectrum of the two colours likewise differs.

**Poisoning by the Vapour of Benzoline.**—M. Foulerton.—From the *Lancet*.

**Detection of Salicylic Acid in Beer and Wine.**—M. Rose.—From the *Journal of the Chemical Society*.

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*Justus Liebig's Annalen der Chemie*,
Vol. ccxxxvi., Part 3.

**Experimental Examination of the Older and the More Recent Formulæ of Dispersion.**—J. W. Bruehl.—The author concludes that none of the formulæ deduced either from the older or from the more recent theories gives the true expression of the law acting in nature. All are applicable up to a certain degree, and all break down if we attempt to apply them beyond a certain limit.

**Synthetic Experiments with Acet-Acetic Ester.**—L. Knorr.—In this second communication the author discusses the conversion of diacet-succinic ester and acet-acetic ester into derivatives of pyrrol. The readiness with which the components coalesce to form the pyrrol ring seems to the author to afford evidence of the stability of this peculiar arrangement of atoms, as appears, indeed, from the numerous pyrogenous modes of formation.

**Phenazine as the Fundamental Substance of the Colouring Matters of the Toluylen-Red Group.**—August Bernthsen and Hugo Sweitzer.—Among the most interesting results of recent chemical investigation must rank our recognition of the fact that there exist certain so-called "ring-shaped" groups of atoms, like those of benzol, naphthaline, anthracene, and pyridine, which are widely distributed and which are formed with exceptional readiness. Among these a peculiar interest attaches to that ring which exists in anthracene, and which is characterised by having two phenylen groups connected by two groups of atoms, which, in the benzol residues, take up the ortho-position to each other, so that with the carbon atoms in question they form a third ring of six members. Two compounds analogous to anthracene, acridine and thiodyphenylamine, have been investigated in the Heidelberg laboratory. These compounds, like anthracene, produce beautiful colouring-matters; thus chrysaniline is a diamido-phenylacridine, and thiodiphenylamine passes, by the intussusception of amido groups or hydroxyles, into the leuko-compounds of colouring-matters of which methylene-blue is the most prominent representative. Hence it seemed to the authors desirable to examine if other diorthodiphenylene derivatives are capable of existence, and if they also are chromogens. Such a body is phenazine. The authors prove that methylphenazine and phenazine are not merely chromogens, but actually give rise to colouring-matters of importance. The safranines (which contain one phenyl group more than the colouring matters of the toluylene-red group) must be referred to a phenyl derivative of phenazine, or rather of hydrophenazine.

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*Bulletin de l'Association des Elèves de M. Fremy.*
Series 2, No. 7.

**The Recruitment of Science.**—E. Fremy.—In this important address the author summarises his former memoirs on experimental instruction in chemistry; reform in higher scientific instruction; abandonment of scientific careers; the recruitment of science; cast-off savants; the volunteers of science; the organisation of scientific careers and scientific attachés. Of a considerable class of youths he writes that the nature of their minds led them to cultivate science, but instead of this tendency being developed they receive an instruction mainly literary. They might have become savants, but they are made into lawyers and journalists.

**Researches on Ramie.**—E. Fremy.—From the *Comptes Rendus*.

**Action of an Electric Current upon Anhydrous Hydrofluoric Acid.**—H. Moissan.

**Decomposition of Hydrofluouic Acid by an Electric Current.**—H. Moissan.

**New Experiments on the Decomposition of Hydrofluoric Acid by an Electric Current.**—These papers are reproduced from the *Comptes Rendus*, and have been already noticed.

**Influence of Foreign Matters upon the Qualities of a Metal.**—Prof. W. Chandler-Roberts.—An abstract of a lecture delivered in London.

**Determination of Glycerin.**—W. Fox and J. A. Wanklyn.

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*Revue Universelle des Mines, de la Metallurgie, &c.*,
Vol. xx., No. 2, September and October, 1886.

**New Calcium Phosphate.**—G. Hilgenstock.—Crystals obtained from the slags of the Thomas and Gilchrist process were found to be a tetrabasic calcium phosphate.

**Note on the Crystals derived from the Thomas and Gilchrist Slag.**—A. de Groddack and Dr. K. Brockmann.—A crystallographic account of the compound described in the foregoing paper.

**Volumetric Determination of Sulphur in Sulphides Decomposable by Hydrochloric and Sulphuric Acids.**—Fr. Weil.—Already noticed.

**A Procedure for the Direct Separation of Manganese and Iron.**—L. Blum.—Noticed under *Zeitschrift f. Anal. Chemie*.

## MEETINGS FOR THE WEEK.

MONDAY, 14th.—London Institution, 5.
—— Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "Building Materials," by W. Y. Dent, F.C.S.
TUESDAY, 15th.—Institution of Civil Engineers, 8.
—— Royal Institution, 3. "Function of Respiration," by Prof. Arthur Gamgee, F.R.S.
—— Pathological, 8.30.
—— Society of Arts, 8. "Some of Our Colonial Woods,' by Allan Ransome.
WEDNESDAY, 16th.—Society of Arts, 8. "Uses, Objects, and Methods of Technical Education in Elementary Schools," by Henry H. Cunynghame.
—— Meteorological, 7.
THURSDAY, 17th.—Royal, 4 30.
—— Royal Society Club, 6.30.
—— London Institution, 6.
—— Royal Institution, 3. "Molecular Forces," by Prof. A. W. Rücker, F.R.S.
—— Chemical, 8. Ordinary Meeting.
FRIDAY, 18th.—Royal Institution, 9. "Genesis of the Elements," by William Crookes, F.R.S.
—— Geological, 1. (Anniversary).
SATURDAY 19th.—Royal Institution, 3. "Modern Composers of Classical Song—Jensen, Lassen, Holstein, Berlioz, and Wagner," by Carl Armbruster.

THE CHEMICAL NEWS.

Vol. LV. No. 1421.

## CONTRIBUTIONS TO THE METALLURGY OF BISMUTH.*

By EDWARD MATTHEY, F.C.S., Assoc. Roy. Sch. Mines.

§ 1. *Bismuth: its Separation from Gold, and its Refining Action upon same during the Process of Separation.*—In bringing the above subject under notice, it is necessary to allude to some of the facts distinguishing this very interesting metal.

Bismuth, in some of its important characteristics and reactions, resembles lead. And one of the chief points of resemblance between these metals is their ready oxidation, and their absorption by bone-ashes or wood-ashes whilst so oxidised. I refer, of course, to the process of cupellation.

This ancient and serviceable process, still employed universally for the separation of gold and silver from lead, is equally applicable to bismuth, if associated with these precious metals; and, like lead, bismuth may be readily employed as a vehicle or means of collecting gold and silver from their ores in reduction processes; but its comparative cost accounts for its non-employment in this respect.

Commercially speaking, bismuth differs from lead in its greater value, lead being worth at present £13 to £14 per ton,† whilst bismuth realises between £700 and £800 per ton; this high value being due to its greater rarity and to its limited and special uses.

As is well known, bismuth ores are frequently auriferous; and one of the points which it is my desire to bring under notice is the effectual separation of the gold from bismuth by a rapid and efficacious process.

Of course, nothing could be easier than to separate these two metals by the ordinary process of cupellation. The gold, by these means, is at once rendered available, but with the drawback that not only is there a very considerable loss of bismuth by volatilisation during the cupellation, but the subsequent recovery of the metal, which in the state of oxide has been absorbed by the cupel, is rendered necessary, involving a tedious and troublesome smelting operation, the employment of expensive fluxes, and a further considerable loss of metal.

Bearing in mind the close resemblance of bismuth to lead in its behaviour in the cupellation process, I directed my attention to its separation from gold by means of the addition of a small proportion of zinc—a method known as the Parkes process, as employed for the separation of silver from lead. And this I found successful, the natural separation of these two metals during the process of cooling proving to be similar in both cases.

The operation is carried out by me as follows:—

The bismuth holding the gold is melted at the ordinary temperature, about two per cent of melted zinc is then added, and the whole brought to a dull red heat. The alloy is then well stirred, and the temperature gradually lowered. When at a black heat the slight crust formed on the surface is skimmed off and the metal again treated with a further quantity of zinc at the higher temperature. *The whole of the gold* will be found in these skimmings, and the bismuth will be thus freed from it.

The skimmings, consisting of bismuth, gold, and zinc, and zinc oxide, I now treat by a process which quickly renders the gold available, and at the same time has the effect of *refining* the gold from all impurities excepting silver during the actual process of extraction.

This small proportion of bismuth litharge and its charge of gold is fused in a clay crucible with a little borax, and allowed to cool down in the crucible, or it is poured into a mould with the bismuth litharge, which being perfectly liquid, allows the metallic gold to separate by its own gravity, and during its fusion absorbs any base metals associated with it as oxides. *The bismuth litharge, in fact, acts as a refining agent to the gold*, which, when cold, is detached from it. This bismuth slag is broken up, refused with a little metallic bismuth, and is so freed from the last trace of gold which is collected by the bismuth, and subsequently extracted. The bismuth litharge so freed from gold is then reduced by fusion with carbon to its metallic state.

The quantity of bismuth litharge holding the gold is exceedingly small in proportion to the bulk of metal originally treated, as the figures hereinafter given will show; but, by this process the bismuth is at once freed from its gold contents with little time, labour, or expense.

I have continuously carried out this method of treatment with the most satisfactory results. It will only be necessary to take the figures of one operation as an illustration.

A quantity of 9483 lbs. of bismuth, holding about one per cent of impurity, and 12·5 ounces of gold per ton (equal to 53·5 ounces in the bulk), was so treated, and of this nearly 9000 lbs. was immediately rendered available for commercial use, the skimmings, which amounted to 658 lbs. (7·30 per cent of the bulk), *containing the whole of the gold*.

These skimmings I oxidised by means of nitric acid, thus obtaining the greater proportion of the bismuth and what little copper there was in solution, from which the bismuth was precipitated by the ordinary method, care being taken to saturate the nitric acid by extracting the greater portion of the bismuth as nitrate, so as to leave a portion of the bismuth as oxide with the gold in order to refine it from the impurities existing as oxides when fused with it. This residue, collected and dried, was, when dried, fused in clay crucibles, with a small quantity of borax, yielding the full amount of gold shown by assay.

As before stated, in these fusions the metallic gold separates from the bismuth litharges, and descends to the bottom of the crucible by its own gravity. The liquid and supernatant bismuth litharge floats upon it and breaks away readily when cold, the gold so obtained being associated only with silver, both metals being in fact *refined by the action of the bismuth litharge*.

§ 2. *Separation of Bismuth from Lead.*—The difficulty surrounding the treatment of bismuth associated with other metals by any rapid or comprehensive process is well known to the metallurgical chemist. I believe I am correct in stating that hitherto the only process employed for the refining of bismuth on the Continent—notably in Saxony, the chief continental source of this metal—has been that of chlorination and subsequent precipitation, a process tedious in itself, and involving much plant and labour in comparison with the quantities of metal operated upon.

Rapidity of production with a minimum margin of loss, in order to free the metal from its impurities and render it marketable as quickly as possible, being a great desideratum, induced me to turn my attention to its refining by dry processes. In carrying this out I have found present most of the metals which are easily seized by and become associated with the bismuth itself during the process of reduction from its ores,* such as antimony, arsenic, tellurium, lead, copper, &c., all of which I have successively and successfully dealt with.

It is not my intention in this paper to describe the processes adopted for the elimination of these several metals, but to confine myself to the separation of lead, the presence of which especially presented at first great difficulties.

* A Paper read before the Royal Society, Feb. 10, 1887.

† June, 1886.

* See Table of Analyses herewith.

As stated above, I have found that I can separate one by one the metals mentioned above, all of which have been associated with crude bismuth which has come under my notice. In this, success though gradual has been complete; but I was still confronted by the fact that the lead alloy was retained by the bismuth with a most characteristic persistency, which seemed to defy all efforts of separation excepting by tedious wet or acid processes.

The amount of lead existing in the bismuth I operated upon, after freeing it by dry processes from its other impurities, varied from 2 to 10 per cent.

Bearing in mind the respective fusing-points of lead and bismuth, it occurred to me that, as alloys of bismuth and lead fuse at a temperature considerably lower than that of bismuth itself, separation would possibly take place between the two metals at a certain point of cooling: I therefore made the following experiment:—

Taking a quantity of bismuth (about 10 cwts.), holding 11·5 per cent of lead, and fusing same, I allowed the metal to cool until the major part of it had crystallised, then removing the fluid portion.

The residue showed by assay only 6·35 per cent of lead, pointing at once to the partial separation I had hoped for.

These crystals again similarly treated showed only 3·75 per cent of lead.

The operation repeated gave crystals with only 2 per cent of lead, and a fourth crystallisation brought this down to below 0·5 per cent.

As a matter of possible interest I subjoin the progressive results during the crystallising operations of several lots up to the point of bulking, and of finally separating every trace of lead:—

*Bismuth holding 14·6 per cent Lead.*

| | | | |
|---|---|---|---|
| 1st | crystallisation gave | crystals holding | 9·8 p. c. of lead. |
| 2nd | ,, | ,, | 5·1 ,, |
| 3rd | ,, | ,, | 3·8 ,, |
| 4th | ,, | ,, | 2·5 ,, |
| 5th | ,, | ,, | 0·4 ,, |

*Bismuth holding 12 per cent Lead.*

| | | | |
|---|---|---|---|
| 1st | crystallisation gave | crystals holding | 6·2 p. c. of lead. |
| 2nd | ,, | ,, | 4·2 ,, |
| 3rd | ,, | ,, | 1·4 ,, |
| 4th | ,, | ,, | 0·4 ,, |

*Bismuth holding 7·6 per cent Lead.*

| | | | |
|---|---|---|---|
| 1st | crystallisation gave | crystals holding | 4·8 p. c. of lead. |
| 2nd | ,, | ,, | 3·8 ,, |
| 3rd | ,, | ,, | 0·8 ,, |
| 4th | ,, | ,, | 0·4 ,, |

*Bismuth holding 11 per cent Lead.*

| | | | |
|---|---|---|---|
| 1st | crystallisation gave | crystals holding | 5·5 p. c. of lead. |
| 2nd | ,, | ,, | 2·5 ,, |
| 3rd | ,, | ,, | 1·0 ,, |

*Bismuth holding 5·6 per cent Lead.*

| | | | |
|---|---|---|---|
| 1st | crystallisation gave | crystals holding | 2·0 p. c. of lead. |
| 2nd | ,, | ,, | 0·7 ,, |
| 3rd | ,, | ,, | under 0·5 ,, |

*Bismuth holding 5·3 per cent Lead.*

| | | | |
|---|---|---|---|
| 1st | crystallisation gave | crystals holding | 1·8 p. c. of lead. |
| 2nd | ,, | ,, | 0·6 ,, |
| 3rd | ,, | ,, | under 0·5 ,, |

Having attained this point, I worked upon several large quantities of metal—with practically the same results—finally succeeding by a continuation of the process in eliminating every trace of lead.

By the above it will be seen that the process becomes an exceedingly simple one, large quantities being treated at one time, involving little or no loss, and occupying hours, instead of possibly weeks.

To illustrate the facilities of the separation of lead and bismuth alloys, I give the following figures from metal holding originally five per cent of lead.

10,675 lbs. produced, in the course of six to seven crystallisations, 9306 lbs. of available bismuth, the residue 1118 lbs. holding 40 per cent of lead, so that from a quantity of nearly five tons of bismuth and lead allow only about half a ton remained, holding practically the whole of the lead; the bulk of the bismuth separated by simple crystallisation holding traces only of lead, which, if necessary, could be readily eliminated by further crystallisation. From these facts it is apparent that the separation of these two metals can be effected by turning to account their *relative fusing points.*

*Recapitulation of foregoing Experiment.*

10,675 lbs. leady bismuth, holding five per cent lead, yielded 9306 lbs. of good commercial bismuth by the crystallisation process, or within six per cent of the total contents of pure bismuth.

Leaving for subsequent treatment—

Of alloy, holding 40 per cent of lead, 1188 lbs., which is equal to 11·13 per cent of the whole weight of metal treated.

*Average Analysis of the Bismuth Ores worked upon.*

| | |
|---|---|
| Bismuth | 44·57 |
| Lead | 2·35 |
| Antimony | 0·64 |
| Arsenic | 1·26 |
| Moldbdenum | 5·02 |
| Tellurium | 0·17 |
| Iron | 5·25 |
| Manganese | 0·05 |
| Copper | 0·24 |
| Tungstic acid | 2·45 |
| Alumina | 0·18 |
| Magnesia | 0·09 |
| Lime | 0·81 |
| Carbonic acid | 1·47 |
| Sulphur | 3·77 |
| Insoluble earthy matter, chiefly silica | 23·12 |
| Water | 3·37 |
| Oxygen in combination and loss | 5·19 |
| | 100·00 |

## SEPARATION OF MERCURY AND PALLADIUM FROM EACH OTHER AND FROM LEAD, COPPER, AND BISMUTH.

By TH. ROSENBLADT.

The behaviour of the alkaline thiocarbonates to certain sulphides of the IV. and V. group is remarkable, and especially to the metals which form complicated ammonium compounds, *i.e.*, cobalt, nickel, mercury, and palladium. These sulphides dissolve in potassium thiocarbonate in considerable quantities, so that this solubility can be utilised both in qualitative and quantitative determinations. From a thiocarbonic solution of palladium and mercury, the latter only is precipitated by carbonic, whilst the palladium remains in solution.

The author explained in the *Journal of the Petersburg Chemical Society* for 1885 how cobalt and nickel sulphides can be easily separated by potassium thiocarbonate from the remaining sulphides of the IV. and from the hydrates of the III. group.

In analogy with these investigations he has now applied the reagent in question to the V. group, the results of which experiments are here laid down. Potassium thiocarbonate solution (or, briefly, thiosolution) is prepared

by dissolving 1 part of sulphur in 2 parts of carbon disulphide, adding 15 parts caustic potash lye of sp. gr. 1·13, and digesting the mixture for some days in a glass bottle with frequent shaking, until the liquid takes an orange colour. It is then decanted off, and the residue is again treated with 8 parts of potash lye. If the carbon disulphide in the bottle appears colourless more sulphur must be dissolved and the liquid obtained can be used for the further preparation of the reagent. The orange liquids obtained are poured together, allowed to settle, filtered, and are then ready for use.

On mixing solutions of mercuric and palladium chloride and heating them with thio-solution in a beaker, the result is a clear liquid without sediment. Through this solution there is passed washed carbonic acid until all the mercury sulphide is precipitated. The deposit is placed in a double filter, previously dried at 101°, washed sufficiently, and freed from sulphur by treatment with carbon disulphide in a Soxhlet apparatus. The filtrate, after treatment with carbonic acid, is mixed with hydrochloric acid until it has an acid reaction. On the application of heat palladium sulphide is, in course of time precipitated, collected on a filter, washed, dissolved in *aqua regia*, the excess of acid is evaporated off, the residue is taken up in water, filtered, almost neutralised with sodium carbonate, a sufficiency of solution of mercuric cyanide is added, and a gentle heat is applied until the liquid no longer smells of cyanogen. The precipitate is collected, washed, dried, strongly heated in a Rose's crucible (previously tared), and finally let cool in a current of hydrogen.

In a corresponding manner mercury may be separated from lead, copper, and bismuth, but not from cadmium. Mixtures of mercury and silver may also be separated from the same metals.—*Zeitschrift Analyt. Chemie* (vol. xxvi., p. 15).

## THE APPLICATION OF OXALIC ACID FOR THE SEPARATION OF VARIOUS METALS.

By C. LUCKOW.

If oxalic acid is added to the solutions of different common metals—neutral or faintly acid—there are produced in the majority of such solutions precipitates of insoluble or sparingly soluble oxalates. In a few cases only there takes place no separation of insoluble oxalates, and the solutions remain clear.

This latter case occurs in the solutions of the alkali-metals, and those of the higher compounds of some metals rich in electro-negative constituents, in which hydrated alkalies throw down hydrates corresponding to the sesqui- and peroxides, and in which such hydrates form compounds with a metallic acid. A precipitation of insoluble oxalates does not occur in the solutions of neutral salts of the alkaline metals, and in the solutions of chrome, aluminium, iron, manganese, uranium, and tin oxides, as well as of chromic, manganic, and antimonic acids, and of the acids of arsenic.

This behaviour of the oxalates affords means not only of distinguishing the various stages of oxidation of the above acids, but also of separation, qualitatively and quantitatively, of the metals in question in their higher compounds from a great number of other metals. Setting aside gold and platinum we find that among the metals of group VI. stannous oxide and antimony teroxide are separated from their solutions by oxalic acid, whilst no precipitation ensues in the solutions of stannic oxide, antimonic acid, and of the arsenic acids. All the metals of group V. are precipitated by oxalic acid. The oxalates of lead, bismuth, silver, copper, and mercury, both in their maximum and minimum compounds, are almost insoluble; cadmium oxalate is sparingly soluble. Copper, and indeed all other metals, should be thrown down only from hot liquids, preferably by a boiling solution of oxalic acid, or by adding to the boiling solution a sufficiency of finely-pulverised oxalic acid, as the precipitates in boiling solutions subside more rapidly. After the liquid has become clear it is filtered by decantation, so that the least possible quantity of the precipitate is brought upon the filter. The two portions of precipitate (that on the filter and that on the beaker) are then dried, placed in a porcelain crucible, and heated, very cautiously at first, and finally more strongly after the addition of a little nitric acid. Small quantities of copper oxide can be easily converted into oxide; large quantities are inconvenient on account of the gases evolved during the decomposition of the oxalates, which may occasion loss by projection.

The silver salt enters into decomposition at 110°, and detonates if heated more strongly. The mercuric salt is decomposed at 163° somewhat violently into mercurous salt and carbonic acid. Instead of decomposing oxalic acid in its salts by heat alone, it may be destroyed by heating with strong sulphuric or phosphoric acid, with permanganic acid, chromic acid, or with chlorine in an alkaline solution.

As for the metals of group IV., oxalic acid throws down nickelous, cobaltous, manganous, ferrous, and uranous oxides, and also zinc oxide from their neutral or moderately acid solutions as sparingly soluble oxalates. In this group, consequently ferrous, manganous, and uranous oxides may be separated, by means of oxalic acid, from the corresponding higher oxides. The faintly rose-coloured cobalt oxalate and the dull green nickel oxalate much resemble the copper salt in the fineness of the precipitates. Both are very sparingly soluble. Rather more soluble is the lemon-yellow, very stable ferric oxalate, and the manganous salt, which is almost white and settles readily.

The zinc salt is most readily and completely separated by evaporating its solutions mixed with a slight excess of oxalic acid. This behaviour of the zinc salt must be kept in mind in quantitative analyses. The complete separation of all the precipitates produced by oxalic acid is much promoted by the time allowed. The metals of group IV. require more time than those of group V. If to the solutions supersaturated with oxalic acid acid there is added a solution of ammonium chloride or nitrate, the separation of the insoluble oxalates is much promoted. A rapid and complete separation of all these salts is effected by evaporating down the solution with a slight excess of oxalic acid, and taking up the soluble matters in a little water. A volatilisation of volatile chlorides under these circumstances does not take place if oxalic acid is present in excess, even in case of arsenious compounds. Dilute sulphuric and nitric acids do not appreciably increase the solubility of oxalates which are insoluble in pure water, and in dilute oxalic acid. Hydrochloric acid, even if dilute, has a decidedly solvent action. Similar is the action of strong oxalic acid upon various insoluble oxalates. Many of the insoluble oxalates combine with the alkaline oxalates to form soluble double salts. Exceptions are the strontium, barium, calcium, silver, lead, and mercurous salt. The lead and the mercuric salt dissolve in hot solutions of alkaline oxalates, but separate out again on cooling or dilution. The barium, magnesium, and mercuric salts are soluble in ammonium chloride. The non-volatility of the soluble oxalates is of importance, as evaporation is the quickest, simplest, and most certain method of separating the soluble compounds quantitatively from the insoluble. In such solutions the oxalic acid must be present in slight excess. If the evaporated residue is treated with water the soluble oxalates are dissolved without decomposition, and may then be separated from the insoluble by filtration.

Ammonia produces no precipitates in the solutions of antimonic and antimonious acids, whilst precipitates of oxides or of basic salts are formed in the oxalic solutions of stannic, ferric, uranium, chromium, and aluminium oxides. Alkaline phosphates and borates, which, like

ammonia, precipitate all these solutions in the absence of oxalic acid, occasion no deposits in its presence. This behaviour of tin and antimony solutions with ammonia affords a simple means for the separation of the two metals. Even in solutions containing both the tin is thrown down free from antimony if the solution contains sufficient oxalic acid or ammonium oxalate, or if the precipitated tin oxide is dissolved in hydrochloric acid, mixed with oxalic acid, and re-precipitated with ammonia.

If we have to examine an alloy of tin, or antimony, or of both, with lead, copper, zinc, or iron, the comminuted sample is dissolved in a small excess of aqua regia, oxalic acid is added to the boiling solution so long as a precipitate is produced, the insoluble oxalates are allowed to settle on cooling, or the solution along with the precipitate is evaporated to dryness on the water-bath and taken up again in a little water. The separation of the precipitate from the liquid is best effected by decantation through a double filter, bringing upon the filter as little as possible of the precipitate. In quantitative operations the precipitate and the filter are freed from soluble portions by means of a dilute solution of oxalic acid, and both are then dried and cautiously ignited. In the solution are found the tin, iron, and antimony if its conversion into antimonic acid has been complete, and the arsenic as arsenious or arsenic acid. As various oxalates are not absolutely insoluble in water and dilute oxalic acid, traces of them may be found in the solution containing the tin, antimony, and iron, and must be considered in accurate quantitive operations.

In the treatment of the ores, alloys, &c., with aqua regia, it is well, in case antimony is present in large quantity, to mix the solution, before adding the oxalic acid, with chlorine until a distinct and permanent odour of chlorine is perceptible, in order to make sure that all antimony is present as antimonic acid. In presence of zinc it is safest either to evaporate down the solution (after addition of oxalic acid) upon the water bath, or to allow the same oxalic solution, mixed with ammonium chloride or nitrate, to stand for some hours.

In order not to introduce an excess of acid 0·1 grm. of the ore or alloy requires 1 c.c. aqua regia made up of 3 to 4 vols. hydrochloric acid, sp. gr. 1·2, and 1 vol. nitric acid of the same sp. gr., and that this 0·1 grm. requires twice the weight of crystalline oxalic acid $(COOH)_2+aq.$ in order to convert all the dissolved metals into oxalates. If sparingly soluble chlorides or sulphates separate out in the solution, they may be transformed into the corresponding oxalates by boiling with a slight excess of oxalic acid.

If alloys containing tin are treated with nitric acid, the supernatant liquid evaporated to expel nitric acid, the residue or its insoluble portion moistened with a little hydrochloric acid, digested with a strong solution of oxalic acid until the hydrochloric acid is expelled, oxide is dissolved, whilst any metals present forming insoluble oxalates pass into the precipitate. Antimonic acid prepared with strong nitric acid does not possess this property, but the meta-antimonic acid formed by the action of water on antimony perchloride. Solutions of antimonic acid mixed with oxalic acid remain, therefore, clear on dilution with water. It is possible that this different behaviour of tin oxide and antimonic acid may lead to a separation of the two metals.—*Zeitschrift Analyt. Chemie*, vol. xxvi., p. 9.

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Bacillus Phosphorescens.—A luminous bacillus has been studied by Dr. Otto Hermes, at the Berlin Aquarium. If in contact with air it gives out in the dark a peculiar bluish-green light, which reminds the observer of the electric light, and which can be communicated to dead fishes and to sea-water. At temperatures exceeding 40° the bacillus loses its luminous property. If the phosphorescence has been transferred to sea-water it disappears in twenty-four hours. Fresh water cannot be rendered luminous by the bacillus.

## ON THE ESTIMATION OF SULPHUR IN SOLUBLE SLAGS.

By E. D. CAMPBELL.

THE following process may be of enough interest to some of your readers—especially iron and steel chemists—to be worth publishing. I have found the process very rapid and accurate in my work as chemist for this Company.

The estimation of sulphur in soluble slags, or slags decomposed by hydrochloric acid: 0·5 grm. of the finely-pulverised slag is introduced into a cold solution made by taking 25 c.c. hydrochloric acid, sp. gr. 1·19, adding 50 c.c. water and 5 c.c. bromine. A little free bromine is left on the bottom of the beaker. The solution is allowed to stand cold for a few minutes and then gradually raised to a boil, and the boiling continued until the bromine is entirely driven off. The solution is then filtered, a solution of barium chloride added, the whole nearly neutralised with ammonium hydrate, and boiled until the barium sulphate has settled to the bottom. The barium sulphate is then filtered off, washed, ignited, and weighed as usual.

Ohio Iron Company, Zanesville, Ohio,
February 3, 1887.

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## ON THE EXTRACTION OF VANADIUM AND CHROMIUM FROM IRON ORES, PARTICULARLY FROM MAGNETITE.

By EDO CLAASSEN.

IN all treatises on the extraction of vanadium from iron ores which have come into my hands, it is recommended to use the ore for the melting process with sulphur and soda, or with saltpetre and soda, in a very finely pulverised and bolted state; in a few places a repetition of the melting is spoken of as a sure means of getting out all the vanadium present in the ore. The result may be satisfactory if iron ores, such as limonite, which are easily converted into impalpable powders, are used. In cases, however, where ores of considerable hardness, like magnetite, are to be extracted and analysed, the pulverisation alone will not, as many experiments made by me have proved, bring the substance to be operated upon into such a form and condition that, after melting, even if the work is repeated several times, the whole of the vanadium present can with certainty be expected to be transformed into a combination soluble in water.

The chief object, therefore, of my experiments described below was to find out in cases where hard ores, for instance magnetite, are to be dealt with, a short and simple way to bring these into the condition of the finest powders. Mechanical power proved to be insufficient for this purpose, as samples of magnetite brought into a very fine powder were, after ignition with soda and saltpetre, as also with soda and sulphur, and extraction with hot water, still partly magnetic, and, as was shown by special tests, they still contained some vanadium. The following method was finally resorted to, and it gave the desired result in a perfectly satisfactory way:—A quantity of very finely pulverised magnetite was mixed in a capacious dish with an equal weight of water, and then with double its weight of sulphuric acid of 1·840 sp. gr.; the contents of the dish became quite hot, and hence it was thought advisable to cover the vessel, so that any loss of substance might be avoided. When the reaction had ceased, the mixture in the dish was found to be in a nearly dry state. It was now transferred into a platinum crucible and heated, at first slowly, and then after a time with a considerable increase of heat, until the water, then the sulphuric anhydride, and at last the sulphur dioxide formed, were entirely gone. The residue in the crucible, now

probably being the oxidised ore, formed an impalpable powder of a red colour, and of the greatest fineness. As will be shown below, it was in exactly the state of division wanted. I separated it into two parts and treated them as follows :—

I. *Treatment with Soda and Sulphur, &c.*—One portion of the powder was mixed with six times its weight of equal parts of soda and sulphur, then brought into a porcelain crucible, which was now well covered and exposed to gradually increasing heat, until most of the free sulphur was volatilised, *i.e.*, until a flame of burning sulphur was no longer visible outside the crucible. When nearly cold the contents of the crucible were thoroughly extracted with hot water, then filtered and the filtrate acidulated with dilute nitric acid, carefully avoiding loss in consequence of the escape of gas, and then set aside for some time. The liquid was now separated by means of a filter, the precipitate on it washed several times with water, and then brought to perfect dryness. By treating the dry precipitate with carbon disulphide, the free sulphur was easily removed, leaving the vanadium sulphide as a chocolate-brown powder. This, together with the filter, was incinerated in a porcelain crucible, the residue from the evaporated filtrate obtained above, in which there is always a small amount of vanadium present, added to it, and also a small quantity of soda, and the whole ignited. The melted mass, poured on a fragment of porcelain, showed, after cooling, a dark bluish-green colour, *caused by some sodium manganate present.* It was extracted with hot water, the filtered liquid, contained in a flask, mixed with a good deal of ammonium nitrate and boiled, until the smell of ammonia had nearly disappeared. If, after another addition of a little ammonium nitrate, a smell of ammonia is again produced, some more should be added, and the boiling, as well as the addition of a new portion of this salt, should be continued until no smell is evolved after again operating in the same way. Not a trace of the vanadic acid is reduced in this way, which is often the case when neutralising is effected by dilute nitric acid, thus causing the escape of a certain amount of vanadium. However, instead of adding ammonium nitrate, it may be allowed, in cases where a small loss of vanadium is not objected to, to make use of the old method just mentioned of neutralising the alkaline liquid by dilute nitric acid, provided the mixing is done with great care, with constant stirring, always keeping in mind that the reaction of the liquid should never, not even partly or for a moment, turn acid, but always remain at the end a little alkaline.

The liquid, thus treated with ammonium nitrate, was filtered, precipitated with neutral lead acetate (or nitrate), the precipitate washed with water, put together with the filter into a flask, mixed with a sufficient quantity of chlorhydric acid and alcohol, and digested for some time. The precipitate formed by this operation was separated from the green liquid, the filter washed with alcohol, the alcoholic liquids united, evaporated or distilled in a beaker or flask, the remnant mixed with water, treated with hydrogen sulphide, filtered, concentrated by evaporation, poured into a wide porcelain crucible, evaporated on the water-bath, perfectly dried, and ignited. The remaining vanadium pent-oxide, which is mostly impure, and generally contains a little vanadium oxide, gave, repeatedly moistened with a solution of ammonium nitrate and ignited and then extracted for purification with an ammonium carbonate solution or with ammonia, a liquid which, when filtered, evaporated and ignited again in a weighed crucible, left the exact amount of all the vanadium pentoxide present.

The residue on the filter left after the lixiviation of the melted mass obtained by the treatment with soda and sulphur was subjected once more to the same melting process and to all the subsequent operations, for the purpose of showing that all of the vanadium was extracted by *but one* process. The result was a good one, as only a trace of vanadium pentoxide was obtained. The residue left the second time on the filter after melting and lixiviation was then treated as follows :—It was dried, extracted with carbon disulphide, and digested with concentrated chlorhydric acid, which dissolved but a little of it, giving a solution not containing any vanadium or chromium. Most of the residue left here was then by digestion with concentrated nitric acid brought into solution, in which hardly more than a trace of vanadium and no trace of chromium were ascertained. It may be stated here that by the operations just described all the chromium of the ore was left undissolved ; all of it was therefore evidently to be looked for in the small balance of the ore now left after treatment in the above manner. This balance was melted after drying for the extraction of the chromium and also of the vanadium, which had perhaps escaped the solvents, with six times its weight of equal parts of soda and saltpetre, the melted mass lixiviated with hot water and treated as described below under II. While all the chromium of the ore could be stated to be present in the solution, only traces of vanadium could be found in it. I think the above experiments prove clearly that by Treatment I. all the vanadium of the ore finds its way into the solution, while all the chromium is left undissolved. This method of extracting and separating the vanadium is therefore highly to be recommended, particularly if the estimation of this element only is the point aimed at. If, however, it is the object of the analysis to determine the quantity of the chromium as well as that of the vanadium, it may be equally or even more advantageous to make use of the mode of extraction described below under II., which affords nearly as good results, as regards the separation of vanadium, as I.

II. *Treatment with Soda and Saltpetre, &c.*—The other portion of the ore, treated with concentrated sulphuric acid, &c. (see above), was mixed with six times its weight of equal parts of soda and saltpetre, ignited, and perfectly extracted with hot water. The residue was subjected once more to the same operation, and it was only the solution of this last melted mass that was used for the detection and estimation of any vanadium and chromium still left in it. For this purpose it was heated with such an amount of ammonium nitrate that, when the smell of ammonia had disappeared, the addition of a new portion of that salt did not produce it again. The liquid was now precipitated by neutral lead acetate, the precipitate collected on a filter, washed thoroughly, and while still moist digested with chlorhydric acid and alcohol ; the filtrate evaporated to remove, besides the alcohol, most of the acid ; then, after dilution with water, treated with hydrogen sulphide, filtered, evaporated, and ignited. The residue, containing all the vanadium and chromium brought into solution by the last melting process, was mixed, for the purpose of separating these two elements, with soda and sulphur in the proportion of 1 : 3 : 3, and ignited until almost all free sulphur was gone. When cold, the crucible with its contents was put into boiling water ; after filtering, all the chromium present was found on the filter, and all the vanadium in the solution. The filter was incinerated, and the residue mixed with six times its weight of equal parts of soda and saltpetre. After melting, the mass was dissolved in hot water, the solution filtered and precipitated as usual in form of lead chromate.

The vanadiferous filtrate, however, was acidulated in a beaker with diluted nitric acid and filtered after some time ; the residue on the filter, after drying, was extracted with carbon disulphide, mixed with the evaporated filtrate before obtained, and melted. The melted mass, poured on a piece of porcelain, was dissolved in hot water, filtered, boiled for some time, after addition of ammonium chloride, then filtered again and evaporated so far that, after cooling and stirring for a while, no separation of crystals had taken place. Into this solution a lump of ammonium chloride was deposited large enough not to be dissolved entirely ; the precipitate of ammonium meta-vanadate, which separated after a time, was collected on a filter, washed with a sufficient quantity of a saturated

solution of ammonium chloride, dried, and ignited. For the purpose of purification the remaining vanadium pentoxide, after it was moistened with a solution of ammonium nitrate and ignited, was dissolved in ammonia, and the solution evaporated until ammonia could scarcely be detected by the odour, then filtered, evaporated to dryness, and ignited. Very exact analyses demand the collection of the small amount of ammonium metavanadate always remaining in the filtrate, and this is therefore evaporated to dryness and ignited. The residue is digested with some concentrated ammonia, the solution filtered, and precipitated with alcohol. The precipitate, dissolved in a little water, will give a solution, furnishing, when treated as above, with a lump of ammonium chloride, the small residue of ammonium metavanadate. The ignited mass (see above) may also—and this is a good method, after treatment with ammonia, heating to drive off the excess of ammonia, and filtration—be precipitated by lead acetate. The precipitate is then suspended in water, acidulated with nitric acid, and decomposed by means of hydrogen sulphide.* In this way a filtrate is formed which leaves on evaporation and ignition the whole balance of the vanadium pentoxide.

It was already mentioned before that the purpose of melting the ore for the second time with soda and saltpetre was to determine if any vanadium and chromium, and how much, were not extracted the first time. The result of these operations was that scarcely a trace of chromium and but little more than a trace of vanadium were found, so that, if the work is done in a careful way, a repetition of all the operations will surely be unnecessary.

A comparison of the two methods of treatment described shows that Treatment I. is always to be preferred, if it is desired to estimate only the vanadium, because it furnishes at once a solution free from chromium, and the quantity of vanadium left in the ore is smaller, and, further, because a large porcelain crucible can generally be had more easily than a large platinum one.

It is, however, a fact known to every analytical chemist that platinum crucibles are always preferred to such of porcelain, provided there is no objection to use them. With this point in view, it seemed to me to be both interesting and important to ascertain if an addition of a smaller quantity of soda and saltpetre to the treated ore might suffice to decompose it perfectly. The ore or the residue left each time after the ignition and extraction with water on the filter was therefore subjected to these operations three times: the first time it was made strongly alkaline by means of soda and then mixed with the third part of its weight of saltpetre; the second time the residue on the filter was mixed with the third part of each of soda and saltpetre, and the third time double the quantity of an equal weight of each one was mixed with the residue. The result of the melting processes was that the solution obtained the first time was yellow; that of the second time yellowish, and that of the third time hardly yellowish; and while the amount of vanadium and chromium was the largest in the first solution, there was still an appreciable quantity of both in the second; but a little, however, of both in the third. On comparing this result with that above obtained, when the melting was done once only with a considerable quantity of soda and saltpetre, it seems to me clear that, in order to obtain a good result, it is not only advisable, but necessary, to add to the prepared ore about three times its weight of each of these substances.—*American Chemical Journal*, vol. viii., No. 6.

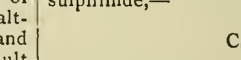
* A precipitate of lead chromate and lead vanadate was suspended in water, acidulated with nitric acid, and treated with sulphuretted hydrogen gas, which decomposed it easily and perfectly. A precipitate, however, of the above lead compounds and of lead sulphate (the last one in considerable excess) did not give an equally good result, although the gas was passed until a strong smell of it remained after standing. It was observed that the smell disappeared again entirely after several hours, although the vessel was well closed, thus showing that a complete decomposition had not taken place. As the same result was obtained after repeated treatment, the precipitate was separated by a filter from the liquid, and both subjected to several tests, which proved that the precipitate contained lead sulphate, lead vanadate, and lead chromate, besides lead sulphide, while in the filtrate sulphuric, vanadic, and chromic acids were found. The above method of decomposing a precipitate of lead vanadate and lead chromate is therefore without doubt a good one only if no lead sulphate, or but a little of it, is present; if, however, a large quantity of it is present, it would be a troublesome and tedious operation to effect the necessary thorough decomposition of the precipitate in this manner. In such a case treatment with chlorhydric acid and alcohol will answer the purpose quickly and satisfactorily.

## INVESTIGATIONS ON THE SULPHINIDES.

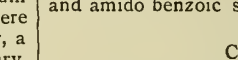
### On Benzoic Sulphinide.*

By IRA REMSEN and A. G. PALMER.

In the first paper† of this series it was shown that the salts derived from phthalic sulphinide are formed by the substitution of the imide hydrogen by metallic elements, and it was suggested that in all probability it would be found that the salts of other sulphinides are formed in the same way. This view has been fully confirmed by subsequent investigations in this laboratory; and the results reached by Noyes‡ in investigating nitro-benzoic sulphinide,—

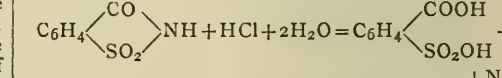


and amido benzoic sulphinide,—



lend additional support to the view.

The sulphinide used in the experiments described below was prepared by oxidation of ortho-toluene sulphamide with potassium permanganate in the usual way. The ortho-toluene-sulphonic acid was prepared by eliminating the nitro-group from nitro-toluene-sulphonic acid by making the diazo-compound and boiling it with alcohol.‖ In regard to benzoic sulphinide a few facts hitherto unknown have been observed. It was found that it can be sublimed without undergoing decomposition, forming thin, elongated, triangular plates. When an aqueous solution of benzoic sulphinide is rendered strongly acid with concentrated hydrochloric acid, and then evaporated almost to dryness on a water-bath, the substance is transformed into ortho-sulpho-benzoic acid, thus:—



In order to prove that the product was really the sulphonic acid it was converted into the sodium salt, which was then treated successively with phosphorus pentachloride and ammonia. Almost the theoretical quantity of the sulphinide was thus obtained. When a solution of the sulphinide is boiled with a concentrated solution of barium hydroxide, ammonia is given off, and the barium salt of ortho sulpho-benzoic acid is formed. From the solution the free acid is easily obtained by precipitating the barium exactly by means of sulphuric acid, and evaporating on the water-bath. From the concen-

* This substance has recently come into some prominence under the name "Saccharin," which is given to it on account of its sweet taste. In the notices of saccharin, even in scientific journals, the statement is constantly made that the substance was discovered by Fahlberg. The statement needs modification. As a matter of fact, the substance came to light in the course of an investigation which Fahlberg undertook at my suggestion, and carried on under my direction, and it was first described in a paper by myself and Fahlberg which appeared in the *Berichte der Deutschen Chemischen Gesellschaft*, Band 12, S. 469. A more detailed account of the investigation was published later in the *American Chemical Journal*, vol. i., p. 426.—I. R.

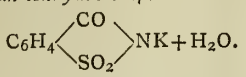
† *American Chemical Journal*, vi., 260.

‡ *Ibid.*, viii., 167.

‖ *Ibid.*, viii., 243.

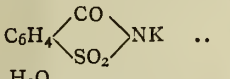
trated solution the free acid separates in white spear-shaped crystals.

*Potassium Anhydro-sulphamine Benzoate,*



A weighed quantity of benzoic sulphinide was dissolved in water, and to it was added a weighed quantity of pure anhydrous potassium carbonate containing the quantity of potassium requisite to form a salt of the above formula. The salt is extremely soluble in water, and it was necessary to evaporate the solution to almost a syrupy consistency before crystals can be obtained from it. On cooling, short, hard, lustrous, prismatic crystals were deposited. These were filtered off and washed with strong alcohol, dried in the air, and analysed.

0·2318 grm. air-dried salt lost 0·015 grm. $H_2O$ at 120°. When heated to 200° it lost no more.

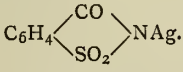


| | Calculated. | Found. |
|---|---|---|
| $C_6H_4\langle^{CO}_{SO_2}\rangle NK$ .. | — | — |
| $H_2O$ .. .. .. .. | 7·52 | 6·90 |

I. 0·2168 grm. anhydrous salt gave 0·0854 grm. $K_2SO_4$.
II. 0·2594 „ „ 0·1022 „

| | Calculated. | | Found. | |
|---|---|---|---|---|
| $C_7H_4SO_3N$ .. | 182 | 82·35 | — | — |
| K .. .. .. | 39 | 17·65 | 17·68 | 17·68 |
| | 221 | 100·00 | | |

*Silver Anhydro-sulphamine Benzoate,*



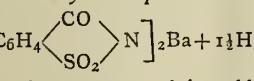
This salt was obtained as a crystalline precipitate by adding a solution of silver nitrate to a warm solution of the sulphinide. It separates almost completely on cooling. It was filtered off, washed with water, and then dissolved in boiling water, in which it is difficultly soluble. On cooling, the salt was deposited in long, white, lustrous needles, which when dry are not changed by light. If a solution of the salt be allowed to stand in the light, it becomes faintly opalescent after a time. The salt contains no water of crystallisation.

I. 0·2817 grm. air-dried salt gave 0·1041 grm. Ag.
II. 0·2685 „ „ 0·0998 „
III. 0·2258 „ „ 0·0840 „

| | Calculated. | | Found. | | |
|---|---|---|---|---|---|
| | | | I. | II. | III. |
| $C_7H_4SO_3N$ | 182 | 62·76 | — | | — |
| Ag .. .. | 108 | 37·24 | 36·95 | 37·17 | 37·20 |

The silver was determined by heating the salt in the air and afterwards in a current of hydrogen.

*Barium Anhydro-sulphamine Benzoate,*



The barium salt was prepared by adding pure barium carbonate to a hot solution of the sulphinide. It is easily soluble in water. From the concentrated solution it is deposited in botryoidal masses. Several attempts were made to obtain it in better form, but without success. If a few drops of the solution containing the salt be slowly evaporated on a glass plate, beautiful radiating needles are formed. After separating the salt from the mother-liquor, it was washed with absolute alcohol and dried in the air. The salt loses weight at 180°, but loses nothing above this.

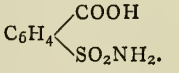
0·2633 grm. air-dried salt lost 0·0265 grm. $H_2O$ at 180°.

| | Calculated for $(C_7H_4SNO_3)_2Ba+3H_2O$. | Found. |
|---|---|---|
| $3H_2O$ .. .. .. | 9·69 | 10·06 |

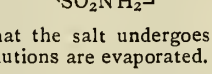
I. 0·2368 grm. anhydrous salt gave 0·1143 grm. $BaSO_4$.
II. 0·2310 „ „ 0·1118 „

| | Calculated. | | Found. | |
|---|---|---|---|---|
| | | | I. | II. |
| $(C_7H_4SNO_3)_2$ | 364 | 72·65 | — | — |
| Ba.. .. .. | 137 | 27·35 | 28·17 | 28·02 |
| | 501 | 100·00 | | |

The results are not satisfactory, but still they are nearer to those required by the composition assumed than they are to those required by a salt derived from the sulphamine acid—



When this salt was first described* the results obtained pointed to the formula—



It seems probable that the salt undergoes slight decomposition when its solutions are evaporated.

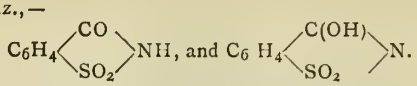
*Attempts to Prepare Ethereal Salts of Benzoic Sulphinide.*

Although Remsen and Fahlberg state* that phosphorus pentachloride does not act upon benzoic sulphinide, it was thought desirable, in view of the results subsequently obtained by Remsen and Stokes,† to study this reaction somewhat more carefully. Accordingly 4 grms. of the sulphinide and an equal weight of phosphorus pentachloride were thoroughly mixed and gently heated over a free flame. The entire mass became liquid. After cooling, methyl alcohol was poured upon the semi-solid material, but apparently no action took place. On warming, the substance dissolved, Water was added, and the excess of alcohol distilled off. On cooling, about a grm. of benzoic sulphinide was deposited. On further evaporation a deposit of short fine needles was obtained, which, after two crystallisations, were obtained in long, delicate, curved needles, which branched off from one another and arranged themselves concentrically in bunches. They were found to melt at 123° to 125°.

Three grms. of the silver salt of the sulphinide were next placed in a small bottle closed by means of a ground-glass plate which could be clamped tightly down, and an excess of methyl iodide added. This was heated on a water-bath at about 100° for six hours. The formation of silver iodide was noticed soon after the heating began. The contents of the bottle were finally treated with hot alcohol, the silver iodide filtered off, the filtrate diluted with water, and heated to drive off the alcohol. On cooling there separated from this solution delicate, curved, somewhat flattened needles, grouped together concentrically, which resembled the substance above described, obtained by treating the sulphinide with phosphorus pentachloride and methyl alcohol. The new substance melted at first at 116° to 119°, but after two re-crystallisations the fusing-point rose to 128° to 129°. Owing to a lack of time and material the question whether the two substances here referred to are identical or not was for the present left unanswered. The ethereal salts of the sulphinide are now under investigation by Mr. R. N. Brackett, and the results will be published during the next academic year. It is hoped that by a careful investigation of these compounds it will be possible to decide

* *Ibid.*, i. 431.
† *Ibid.*, vi., 260.

between the two most probable formulæ for the sulphinide, viz.,—



—*American Chemical Journal*, Vol. viii., No. 4.

## A METHOD FOR THE SEPARATION OF SODIUM AND POTASSIUM FROM LITHIUM BY THE ACTION OF AMYL ALCOHOL ON THE CHLORIDES,

### With some Reference to a Similar Separation of the Same from Magnesium and Calcium.*

By F. A. GOOCH.

(Concluded from page 57.)

In this connection it seems best to include the record of certain experiments looking to the separation of the chlorides of sodium and potassium from the chlorides of magnesium and calcium. The behaviour of magnesium chloride towards amyl alcohol is of interest, both with reference to the problem of separating sodium and potassium from lithium and magnesium when the latter are associated, and as concerns the parting of the alkalies from magnesium alone,—a matter which is by no means perfectly simple,— and experiments (38) to (41) touch upon this topic.

The chlorides of sodium and potassium were weighed, as before, in solution; the magnesium chloride was obtained by dissolving in hydrochloric acid the oxide specially prepared and weighed as such. The process of treatment was identical with just that described for the separation of the chlorides of potassium and sodium from lithium chloride.

The residues of the experiments (38) and (39), in which the separation was made by a single precipitation, carried traces of magnesia; those of (40) and (41) in which, two precipitations were introduced, were found to contain in the one case no magnesia, and in the other an unweighable trace. These results point out a method by which the chlorides of sodium and potassium may be obtained free from magnesia, while the small amounts of the former which pass into solution with the magnesium chloride are capable of accurate estimation; and there seems to be no reason why the separation of these alkaline chlorides from magnesium chloride and lithium chloride occurring together should not be effected in one operation, and the parting of the latter salts brought about by the familiar method of precipitating the magnesia in the cold as ammonium-magnesium phosphate.

Experiments (42) to (48), upon the separation of sodium and potassium from calcium by the action of amyl alcohol on the chlorides, yielded the figures of the following table. The mode of treatment was identical with that of the experiments of magnesia, just described, excepting only the substitution of pure calcium oxide, specially prepared, for magnesium oxide.

| | Weight of NaCl taken. | Weight of KCl taken. | Weight of NaCl+KCl found. | Corrected weight of NaCl+KCl found. | Volume of amyl alcohol used. Residual. I. | Residual. II. | Total. |
|---|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | C.m.³ | C.m.³ | C.m.³ |
| (38) | 0·1030 | 0·1064 | 0·2079 | 0·2100 | 23 | — | 120 |
| (39) | 0·0967 | 0·1024 | 0·1976 | 0·2006 | 33 | — | 100 |
| (40) | 0·1030 | 0·1073 | 0·2071 | 0·2993 | 13 | 11 | 100 |
| (41) | 0·1053 | 0·1093 | 0·2114 | 0·2142 | 12 | 18 | 100 |

| | Weight of MgO taken. | Error in Weight of NaCl+KCl found. | Error in corrected Weight of NaCl+KCl found. |
|---|---|---|---|
| (38) | 0·1000 | 0·0015− | 0·0006+ |
| (39) | 0·1000 | 0·0015− | 0·0015+ |
| (40) | 0·1000 | 0·0032− | 0·0010− |
| (41) | 0·1000 | 0·0032− | 0·0004− |

From these results it is plain that it is a far more difficult matter to dehydrate and dissolve calcium chloride than either magnesium chloride or lithium chloride. The separation of the chlorides of sodium and potassium from calcium chloride cannot be accomplished, for the quantities employed in these experiments, by a single precipitation; but the repetition of the treatment is effective. In the residues of experiments (46) and (47) calcium could not be found by the test with ammonium oxalate. In a case, therefore, in which the separation of sodium and potassium from lithium, magnesium, and calcium in one operation should be desirable, the end may probably be accomplished by means of the process here described.

Certain preliminary experiments with the nitrates of the bases under discussion indicate that these are susceptible

| | Weight of NaCl taken. | Weight of KCl taken. | Weight of NaCl + KCl found. | Corrected weight of NaCl + KCl found. | Volume of amyl alcohol used. Residual. I. | Residual. II. | Total. |
|---|---|---|---|---|---|---|---|
| | Grm | Grm. | Grm. | Grm. | C.m.³ | C.m.³ | C.m.³ |
| (42) | 0·0859 | 0·1126 | 0·2177 | 0·2195 | 20 | — | 100 |
| (43) | 0·1018 | 0·1057 | 0·2217 | 0·2235 | 20 | — | 100 |
| (44) | 0·1096 | 0·0962 | 0·2112 | 0·2130 | 20 | — | 100 |
| (45) | 0·0985 | 0·1018 | 0·2113 | 0·2130 | 19 | — | 100 |
| (46) | 0·0914 | 0·1104 | 0·1968 | 0·2000 | 20 | 15 | 100 |
| (47) | 0·0997 | 0·1100 | 0·2080 | 0·2019 | 3 | 7 | 90 |

| | Weight of CaO taken. Grm | Error in weight of NaCl + KCl found. Grm. | Error in corrected weight NaCl + KCl found. Grm. |
|---|---|---|---|
| (42) | 0·1000 | 0·0192+ | 0·0210+ |
| (43) | 0·1000 | 0·0142+ | 0·0160+ |
| (44) | 0·1000 | 0·0054+ | 0·0072+ |
| (45) | 0·1000 | 0·0110+ | 0·0127+ |
| (46) | 0·1000 | 0·0050− | 0·0018− |
| (47) | 0·1000 | 0·0017− | 0·0008− |

of similar separation by the action of amyl alcohol; and the wide applicability in analytical operations of the general principle involved,—the dehydating of salts by means of amyl alcohol or other liquid of high boiling-point and appropriate solvent action,—can scarcely be a matter of doubt.

## PROCEEDINGS OF SOCIETIES.

### PHYSICAL SOCIETY.

*Annual General Meeting, February* 12, 1887.

Prof. B. Stewart, F.R.S., President, in the Chair.

In opening the proceedings the President regretted that in their Report the Council have to record the loss of one who took a prominent part in the proceedings of the Society,—the late Dr. Guthrie. It was, however, satisfactory to learn that the appeal of the Guthrie Memorial Committee, under the presidency of Prof. Huxley, had been generously responded to.

The Council also learn with regret, from Dr. E. Atkinson, that, owing to pressure of work, he is unable to retain the office of Treasurer to the Society, and desire to express their thanks to him for his past services. Prof. Rücker has consented to be nominated for the office thus rendered vacant, and the Council believe that by his election the connection between the Society and the Normal School of Science (which is so desirable) will be maintained.

The Report of the Council for the year 1886 was read and received, and the following gentlemen were elected Members of the Council for the present year:—

*President*—Dr. Balfour Stewart, LL.D., F.R.S.

*Vice-Presidents*—Dr. E. Atkinson; Prof. W. E. Ayrton, F.R.S.; Shelford Bidwell, M.A., LL.B., F.R.S.; Prof. H. McLeod, F.R.S.

*Secretaries*—Prof. A. W. Reinold, M.A., F.R.S.; Walter Baily, M.A.

*Treasurer*—Prof. A. W. Rücker, M.A., F.R.S.

*Demonstrator*—C. V. Boys, M.A.

*Other Members of Council*—R. H. M. Bosanquet, M.A.; W. H. Coffin; Conrad W. Cooke; Prof. G. Forbes, F.R.S.E.; Prof. F. Fuller, M.A.; Prof. J. Perry, F.R.S.; W. N. Shaw, M.A.; Prof. S. P. Thompson, D.Sc.; C. M. Whipple, B.Sc.; C. R. Alder Wright, D.Sc., F.R.S.

The President proposed the following Resolution:—That at the end of Clause 11 of the Bye-Laws, which says "Every candidate for admission into the Society shall be recommended by not less than three members, to two of which he must be personally known," there be added "When a candidate living abroad is a member of a recognised scientific society, such membership may, subject to the approval of the Council, be held equivalent to the personal knowledge aforesaid." The Resolution was carried, subject to confirmation by a Special General Meeting to be held on February 26th.

A vote of thanks, proposed by Prof. Ayrton and seconded by Prof. McLeod, to the Lords of the Committee of Council on Education, for the use of the rooms and apparatus of the Normal School of Science, was passed unanimously.

The Hon. R. Abercromby proposed a vote of thanks to the officers of the past year for their gratuitous services, which was seconded by Prof. Pickering.

Sir Phillip Magnus proposed a vote of thanks to the auditors, Col. Festing and Prof. Fuller, which was seconded by Mr. Lecky, and passed unanimously.

Mr. J. Brown was elected a member of the Society.

The following communication was then read:—

"*Note on the Tenacity of Spun Glass.*" By E. Gibson and R. E. Gregory.

The authors have experimented on the tenacity of glass rods and fibres made from the same piece of glass. The fibres varied from $\frac{1}{25}$ to $\frac{1}{10}$ m.m., and the rods from about $\frac{1}{2}$ to 1 m.m. in diameter. They find the tenacity per square c.m. of rods increases as the diameter decreases, as in ordinary wires, whereas with fibres this is not shown. Experiments were shown illustrating the methods of working, and the highest tenacity recorded was for a fibre of 0·0340 m.m. diameter, which gave $466 \times 10^7$ dynes per square c.m.—a value about half as great as that for steel wires. The authors refer to Quincke's suggestion that the increased tenacity of small wires is due to surface tension, and may be represented by $W = Ad + Bd^2$, where W is the breaking weight and $d$ the diameter; but their own results with glass do not agree with this formula.

Sir Phillip Magnus asked if the diameters were measured at the point of rupture, if the elongation was determined, and whether the authors were able to suggest any other formula which would express their results?

Mr. C. V. Boys remarked that the tenacity being so much affected by accidental circumstances, such as rate of cooling, no such formula could be expected.

Prof. Rücker, referring to Quincke's experiments, said that the surface tension of metals calculated from them appear improbable.

After some further remarks by the President, Prof. Ayrton, Mr. C. V. Boys, Prof. McLeod, and Mr. Gregory, the proceedings terminated.

## NOTICES OF BOOKS.

*Proceedings of the American Pharmaceutical Association at the 34th Annual Meeting, held at Providence, R.I., September*, 1886. Philadelphia: The Association.

The queries proposed for answer at the next annual meeting belong almost exclusively to the region of pure pharmacy. We notice the question—"To what extent can corrosive sublimate be safely used as an antiseptic?"

The Committee on Legislation give abstracts of State enactments on the sale of "poisons," which must in many cases occasion inconvenience in the arts and in scientific research. Thus we regret to see the sale of the mineral acids encumbered with a cloud of formalities.

A section headed "Assays of Commercial *Abstracts*" made us at first inclined to blame the compositor, but as the peculiar term is frequently repeated, we can only presume that it is a neologism for extracts.

The chapter on pepsine calls to our mind a harrowing observation chronicled in "*Cosmos*." A police official in Paris watched a man collecting *album græcum* in the streets, and feeling curious as to its possible uses, traced him to an eminent manufactory of peptones, where he disposed of his gatherings!

In "Butter and its Substitutes" Mr. E. Scheffer proposes as a method for ascertaining the character of butter as genuine or spurious, to ascertain the solubility in a liquid composed of 40 vols. rectified amyle oil and 60 vols. of "Squibb's stronger ether." Genuine butter, it appears, at 82° F. dissolves in 3 c.c. of this liquid, whilst different samples of "butterine" require 11 and 8 c.c. Unfortunately, chemists in Europe do not known what is meant by "Squibb's stronger ether."

*Manual of Chemical Manipulation, or of Operative Chemistry.* (Manuel de Manipulations Chimiques, ou de Chimie Opératoire.) By Fr. de Walque. Louvain: Aug. Peeters-Ruelens. Paris: Gauthier-Villars. Third Edition. 1887.

The latest edition of this handbook shows a very marked improvement over the previous editions, the most striking and not least valuable alteration being the substitution of

over 350 cuts interspersed throughout the book, for the sheets of illustrations which in the last edition were all collected at the end. In addition to this the whole work has been enlarged and greatly improved: there is, however, a very formidable list of *errata*, which points to a rather hasty correction of proofs.

We are glad to notice that our remarks on the chapter on the production and application of heat have been favourably received. This chapter has been completely remodelled, and due attention given to Fletcher's solid-flame burners and Wiesnegg's furnaces and gas-regulator.

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*Report of the Jury of Group* IV., *Class* 42 (*Chemical and Pharmaceutical Products*), *of the "Exposition Universelle d'Anvers" of* 1885. By Fr. de Walque. Brussels: Alfred Kromont. 1886.

Class 42 in this Exhibition comprised the following materials:—

*a*. Acids, alkalies, and salts of all kinds.
*b*. Various products of chemical industries, such as waxes, soaps, perfumes, tars, varnishes, india-rubber, colours, &c.
*c*. Natural and artificial mineral aërated waters, pharmaceutical products, and patent medicines.

The Report now before us deals in a very comprehensive manner not only with the materials as exhibited, but it also gives descriptions of the various manufactures, pointing out the improvements which have been made, and making suggestions as to what direction further efforts should take. The jury regret, however, that exhibits of pure chemicals were conspicuous by their absence. England we find was poorly represented, although some of the most important houses took part in the exhibition.

The first part of the Report deals with the great chemical industries,—that is to say, the manufacture of soda, which comprises the cycle of operations of sulphur, sulphuric acid, hydrochloric acid, sulphate and carbonate of soda, and chloride of lime. After touching on the Leblanc process we come to that of Messrs. Solvay, and note that this firm exhibited specimens of hydrochloric acid made from common salt during their process, but the jury is of opinion that the cost at present is too high to permit of its being a commercial success. If, however, Messrs. Solvay succeed, as they feel confident they will, it will be the death-blow to the Leblanc process.

In the pages devoted to refined salt we find that the English firms were decidedly in advance of their foreign competitors, both in quality and quantity turned out.

Among the smaller chemical industries we note that Dr. Marquart, of Bonn, had a very excellent collection of crystals of rubidium and cæsium alum.

M. Polier's exhibit of peroxide of hydrogen, made by the reaction of hydrofluoric acid on binoxide of barium, also attracted special attention.

An important subject, which has not yet made much progress, is that of rendering wood and other materials incombustible. Nothing has yet been found better than tungstate of soda for effecting this. The prolonged action of fire on wood, even when protected, eventually effects its decomposition, and the gases escaping catch fire; the carbon, however, which is left behind, does not burn easily when the tungstate has been thoroughly well applied.

Considerable attention has been paid to disinfectants, and the purification of rivers after contamination from chemical works.

The chapter on the manufacture of india-rubber is of great interest; and we next come to pigments and organic colouring-materials, and such like.

Several pages are taken up with a full account of the manner of using the wood Quebracho, containing over 20 per cent of tannin, by a very large German tanner.

The exhibits of natural and artificial aërated mineral waters are next very fully described and comparative tables of analysis given; and finally we have an account of the recent improvements in pharmaceutical products.

The Report as a whole is of great interest, and speaks well for the energy and careful observation of the jury who have issued it.

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## CORRESPONDENCE.

### VAPOUR DENSITY.

*To the Editor of the Chemical News.*

Sir,—Your correspondent J. W. S., who has difficulty with vapour densities, has perhaps too short or too small a capacity of bulb on his vaporimeter, or is attempting to perform the operation in a draughty place. If the bulb be large enough for the volume of vapour, and no air-draughts about, there should be no tendency to draw back until after the operation is over. The sort of vaporimeter made or procurable in England is not very well adapted for its work. I have found it much better to make them, and to blow a bulb of about 25 c.c. capacity on the side tube leading to the air-collecting tube. This is especially useful with a lead-bath, as then any water drawing back from the trough in which the air-measuring tube is inverted will be held, and prevented from going down into the lead so rapidly; it gives time to take out the cork from the top of the vaporimeter.—I am, &c.,

N. S. S.

February 14, 1887.

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## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 1, January 3, 1887.

On a Hydrated Silicon Phosphate.—P. Hautefeuille and J. Margottet.—On submitting to the action of heat a solution of silica in phosphoric acid, there is obtained a compound which crystallises in four distinct forms, and which answers to the formula $PO_5SiO_2$. If kept for some days at 125° in a platinum crucible this solution deposits spherical concretions. These spherical globules, if immersed in strong sulphuric acid, act powerfully upon polarised light. Their composition is $SiO_2,2PO_5,4HO$.

Action of Sulphur upon Ammonia and upon certain Metallic Bases in Presence of Water.—J. B. Senderens.—Ordinary liquid ammonia, into which pure sulphur had been introduced, was left to itself in a closed vessel at about 12°. After three weeks the liquid began to take a slight yellow tint, which passed gradually into a reddish tone, and became in two years of a very decided red. This liquid contained an ammoniacal polysulphide and a hyposulphite. On exposure to the air sulphur was deposited. The alkaline-earthy bases in solution, if heated in closed vessels with sulphur, behave like alkaline oxides. Oxide of silver and litharge, if heated in sealed tubes with sulphur and water, are converted into silver and silver and lead sulphides and sulphates. Under the same conditions mercury and copper oxides, which are entirely insoluble, produce sulphates and sulphides. Ferric oxide is scarcely acted upon by sulphur, and zinc oxide not at all.

Isomerism of Camphols and Camphors; Camphols of Madder, of Borneol, and of Amber.—Alb. Haller.—All the natural camphols are chemically identical, and differ among themselves only by their action on polarised

light. The camphols of madder, of valerian, of N'gai, of Bang-phien, have the same molecular rotatory power to the left $(\alpha)_D = -37°$. The camphor corresponding to the camphols is identical with the camphor of mother-wort. The camphol of *Dryobalanops camphora* has a rotatory power equal to that of the above camphols, but in the opposite direction. The derivatives are identical with those of ordinary camphor. The camphol of amber seems to consist chiefly of a racemic camphol mixed with a dextro-borneol.

Maximum Vapour-Tensions of Sodium Acetate.—H. Lescœur.—The results of the author's experiments have been given in the form of tables.

Preparation of the Isobutylamines.—H. Malbot.—By heating isobutyl chloride, instead of bromide, with ammonia, dissolved, not in ordinary alcohol but in isobutylic alcohol or in water, the author obtains the three isobutylamines in proportions not greatly differing.

Formation-Heat of Certain Potassium Alcoholates.—M. de Forcrand.—This memoir does not admit of useful abstraction.

Certain Points Relative to the Action of Saliva upon the Grain of Starch.—Em. Bourquelot.—At the temperature where water begins to transform starch into a hydrate saccharifiable by saliva at the ordinary temperature, water mixed with saliva exerts a greater action than do water and saliva used in succession.

No. 2, January 10, 1887.

Action of Carbon Chloride upon Anhydrous Oxides.—Eug. Demarçay.—The author examines if the action of carbon tetrachloride can be utilised for the convenient preparation of the anhydrous chlorides. He has readily succeeded with the oxides of chromium, aluminium, titanium, niobium, tantalum, and zirconium, but not with silica. The reaction must take place at temperatures below redness.

On Erythrite.—Albert Colson.—Erythrite should give successively on oxidation a monobasic and a bibasic acid. The author has obtained the monobasic acid in question—erythritic acid.

On Potassium Glycerinate.—M. de Forcrand.—A thermo-chemical paper, not capable of useful abstraction.

The Derivatives of Erythrene.—MM. Grimaux and Cloez.—Not adapted for abridgment.

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*Bulletin de la Société Chimique de Paris.*
Vol. xlvii., No. 1, January 5, 1887.

New Method for Determining Starch and the Different Kinds of Sugar.—Dr. J. Effront.—The liquid is brought to a degree of concentration such that it may contain from 4 to 9 per cent of sugar, and its rotatory power is observed. Ten c.c. of this liquid are mixed with 10 c.c. of ammonia at 22° B. and 5 c.c. of water. The whole is put in a well stoppered flask, holding 300 c.c., and the stopper is attached to the neck by means of a thread. The flask is set in cold water, which is then heated and let boil for forty minutes. The contents, when cold, are poured into a long-necked flask, in which the liquid is concentrated to 5 to 8 c.c. This concentrated liquid is then cooled and poured into a glass plunged into cold water. After having added 10 c.c. of a solution of sodium hypochlorite (at 7 to 8 per cent of active chlorine), the liquid is agitated, and about 2 c.c. of strong hydrochloric acid are added. The mixture is now poured into a graduated cylinder and made up, by the addition of water, to 25 c.c. The rotatory power of this liquid is then determined, bearing in mind that its volume has been increased in the proportion of 1 : 2½. In his experiments the author has employed Soleil's saccharimeter. If after the treatment with sodium hypochlorite there is formed a persistent froth which makes it impossible to read off accurately the volume of the liquid, this froth may be touched with a glass rod dipped in amylic alcohol, when it will disappear at once.

Researches on Antimony Sulphide.—M. Berthelot.—Already noticed.

Formation of Oxalic Acid in Plants.—MM. Berthelot and André.—Already noticed.

A Relation between the Formation of Oxalic Acid and that of the Albumenoid Principles in Plants.—MM. Berthelot and André.—Already noticed.

On the Speed of Dissociation.—H. Lescœur.—The considerations drawn from the speed of dissociation yield valuable information as to the existence of hydrates and analogous compounds, but they can give neither absolute nor relative indications as to the value of the tensions of dissociation. The speed of dissociation, in fact, is not merely a function of the tension of dissociation, but it depends also on the physical condition of bodies, an element which escapes all measurement.

Caprylidine, an Acetylenic Carbide, its Hydration, and the Constitution of Caprylic Aldehyd.—A. Béhal.—Caprylic aldehyd possesses physical properties similar to those of methyl-hexyl-acetone, but the oxidation of these bodies and their reducing powers being different it is convenient to distinguish them. The substance designated by Limpricht and Bouis as caprylic aldehyd is certainly an aldehyd.

Alloys of Platinum, Iron, and Copper.—E. Maumené.—Copper, at high temperatures, has the power of dissolving iron and platinum. The author has obtained a homogeneous button containing 7·43 per cent of iron, 19·65 of platinum, and 72·92 per cent of copper. This alloy is very liable to oxidation.

Determination of Indigo on Textile Fibres.—A. Renard.—Already noticed.

Action of Oenanthol and Oenanthyle Chloride upon Dimethylaniline, in Presence of Zinc Chloride.—V. Auger.—Oenanthol combines with dimethyl-aniline in presence of zinc chloride. The base obtained is readily decomposed by oxidising agents, with separation of the heptyle group. Oenanthyle chloride combines with dimethyl-aniline, forming either a leuko-base or an acetone, according to circumstances.

Separation of Antimony and Tin.—Ad. Carnot.—Already inserted.

Separation of Antimony, Arsenic, and Tin.—Ad. Carnot.—Already inserted.

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*Biedermann's Central Blatt für Agrikultur Chemie.*
Vol. xv., Part 9.

On Dew.—J. Aitken.—The author rejects the theory of Wills and returns to that of Gersten, propounded in 1733, *i.e.*, that dew is derived from the moist earth.

Formation of Mists.—R. von Helmholtz.—The most usual cause of the formation of mists is the adiabatic expansion of moist air; that is, an expansion which takes place alone at the expense of the internal supply of heat of the gas. Two factors come into play which act in opposition to each other—decrease of pressure and refrigeration. The mist-spherules are not formed out of nothing, but require solid or liquid nuclei, which are always present in the atmosphere. It may be concluded from the existence of clouds that that dust is everywhere suspended in the atmosphere. This confirms Tyndall's conjecture that the blueness of the sky is due to such minute solid particles.

Effects of Chilian Saltpetre.—Prof. Magerstein.—A comparison of the results of this manure, when incorporated with the soil and when used as a top dressing.

Chili Saltpetre, its Importance and Application.—Dr. A. Stutzer.—The author, in a prize dissertation,

shows that results satisfactory to the farmer cannot be attained without nitrogenous manures. The farm-yard manure produced on an estate is generally not sufficient for conveying to the crops the needful quantity of nitrogen. He finds sodium nitrate preferable to ammoniacal salts, and still more decidedly to organic nitrogen.

**Comparative Experiments with Chilian Saltpetre and Ammonium Sulphate.**— Prof. Magerstein.— These experiments show that sodium nitrate is the more efficient manure except as regards the production of straw.

**Iron and the Chlorosis of Plants.**—Prof. J. V. Sachs.—The author describes the symptoms of vegetable chlorosis, and recommends the salts of iron as a remedy.

**The "Laktokrit."**—G. de Laval.—This is an apparatus for testing milk, invented and patented by the author. The principle is the liberation of the fatty matter from its emulsive state by an admixture of acetic and sulphuric acid with the aid of heat, and, secondly, the separation of such fat by centrifugal action.

**A Contribution to the Question of the Presence of Nitric and Nitrous Acids in Milk, and the Detection of the Watering of Milk.**—Dr. M. Schrodt.—Milk in its natural state has never been found to contain nitric or nitrous acids. If such are recognised by means of diphenylamine (Soxhlet's process), the presence of well-water may be inferred.

## MISCELLANEOUS.

**Chemical Labels.**—We have just received from Messrs. F. E. Becker and Co. their new book of 330 Chemical Labels, gummed ready for use. The names are very distinctly printed in large type, and the formulæ of the compounds are also given.

**Influence of Time on the Transformation of the Colouring-Matters of Coal-Tar in Presence of Wines.**—M. Cazeneuve.—The chief coal-tar colours employed for colouring wines, acid magenta, Bordeaux red, purple-red, and rocceline red, may remain in certain wines unchanged for years, and may be recognised on analysis. The chemical modifications which wines undergo, such as the settling in new wines, occasion the precipitation of a larger or smaller part of the artificial colouring. The diseases of wine, such as the action of *Mycoderma vini* and *Mycoderma aceti*, occasion the rapid disappearance of the colour.—*Journ. de Pharm.*

## MEETINGS FOR THE WEEK.

Monday, 21st.—London Institution, 5.
—— Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "Building Materials," by W. Y. Dent, F.C.S.
Tuesday, 22nd.—Institution of Civil Engineers, 8.
—— Royal Institution, 3. "Function of Respiration," by Prof. Arthur Gamgee, F.R.S.
—— Society of Arts, 8. "Wrought Ironwork," by J. Starkie Gardner, F.L.S.
—— Royal Medical and Chirurgical, 8.30.
Wednesday, 23rd.—Society of Arts, 8. "Recent Advances in Sewing Machinery," by John W. Urquhart.
Thursday, 24th.—Royal, 4.30.
—— London Institution, 6.
—— Telegraph Engineers, 8.
—— Royal Institution, 3. "The Critics of the Age of Anne," by Edmund Gosse, M.A.
Friday, 25th.—Royal Institution, 9. "Sunlight Colours," by Capt. W. de W. Abney, F.R.S.
—— Quekett Club, 8. (Anniversary).
—— Society of Arts, 8. "New Markets and Extension of Railways in India and Burmah," by Holt S. Hallett, F.R.G.S.
Saturday 26th.—Royal Institution, 3. "Sound," by the Right Hon. Lord Rayleigh.
—— Physical, 3. "Note on Prof. Carey Foster's Method of Measuring the Mutual Induction of Two Coils," by James Swinburne.

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## GENESIS OF THE ELEMENTS.*

By WILLIAM CROOKES, F.R.S., V.P.C.S.

In the very words selected to denote the subject I have the honour of bringing before you, I have raised a question which may be regarded as heretical. At the time when our modern conception of chemistry first dawned upon the scientific mind, the average chemist as a matter of course accepted the elements as ultimate facts. He regarded his elements as absolutely simple, incapable of transmutation or decomposition, each a kind of barrier behind which we could not penetrate. If closely pressed he said that they were self-existent from all eternity, or that they had been individually created just as we now find them at the present day. Or he might argue that the origin of the elements did not in the least concern us, and was, indeed, a question lying outside the boundaries of science.

But in these our times of restless inquiry we cannot help asking what are these elements, whence do they come, what is their signification? We cannot but feel that unless some approach to an answer to these questions can be found, our chemistry, after all, is something profoundly unsatisfactory. These elements perplex us in our rearches, baffle us in our speculations, and haunt is in our very dreams. They stretch like an unknown sea before us—mocking, mystifying, and murmuring strange revelations and possibilities.

If I venture to say that our commonly received elements are *not* simple and primordial, that they have *not* arisen by chance or have *not* been created in a desultory and mechanical manner but have been evolved from simpler matters—or perhaps indeed from one sole kind of matter—I do but give formal utterance to an idea which has been, so to speak, for some time "in the air" of science. Chemists, physicists, philosophers of the highest merit declare explicitly their belief that the seventy (or thereabouts) elements of our text-books are not the pillars of Hercules which we must never hope to pass.

Did time allow I might quote utterances of Dalton, of Prof. Faraday, of Dr. Gladstone, of the late Sir Benjamin Brodie, of Prof. Graham, of Dr. Mills, of Prof. Stokes, of Mr. Norman Lockyer, all pointing in the same direction and all showing that in the course of their researches these servants of Science have been led to think that these same elements are not the final outcome—the be-all and the end-all of chemistry.

The law of Prout, and still more the better-established and far-reaching periodic law of Newlands (since developed by Professors Mendeleeff, Meyer, and Carnelley), seem to presuppose the existence of a genetic relation among the elements.

Philosophers in the present as in the past,—men who certainly have not worked in the laboratory,—have reached the same view from another side. Thus Mr. Herbert Spencer records his conviction that "the chemical atoms are produced from the true or physical atoms by processes of evolution under conditions which chemistry has not yet been able to produce."

And the poet has forestalled the philosopher. Milton ("Paradise Lost," Book V.) makes his Archangel Raphael say to Adam, instinct with the evolutionary idea, that the Almighty had created

> "one first matter all
> Indued with various forms, various degrees
> Of substance."

If we can show how the so-called chemical elements might have been generated we shall be able to fill up a formidable gap in our knowledge of the universe. We have a preponderance of cumulative evidence to prove that both heavenly bodies and living organisms have been formed by evolution. We are seeking now to extend this law to the so-called elements, to the first principles of which stars and organisms alike consist.

If we survey the distribution of the chemical elements we find two very distinct cases. On the one hand we see bodies grouped in definite proportions with other bodies from which they differ exceedingly and to which they are held by affinity, more or less strong. To obtain either of two such bodies in a separate state, that affinity, as every student of chemistry knows, must be overcome. Instances of such association are too common and abundant to need mention. In such cases each of the bodies grouped together has fairly marked properties. One of them, moreover, for the most part has an atomic weight very different from that of the other.

In the second case we find bodies associated with other bodies more or less closely allied to themselves. They are not held together by any decided affinity; they are not combined in definite proportions, and their atomic weights are often almost identical. If we wish to obtain one or more of these bodies in a separate state, the difficulty encountered lies not in the strength of the affinities to be overcome but in the circumstance that whatever reagent we employ acts upon one of the substances in nearly the same manner as it does upon the other. Hence, to obtain one body of this kind entirely separate is an exceedingly tedious and difficult task. Nay, we are sometimes at a loss to decide whether we have before us a really simple body or a mixture of bodies whose properties are almost identical.

The most striking instance of such association is found in the metals of the so-called *rare earths*. These bodies form but a very trifling portion of the earth's crust. They are chiefly met grouped together in a few minerals, such as samarskite and gadolinite, which, so far, have been found in but few localities, and even in those are far from common. These earths form a group to themselves; chemically, they are so much alike that it taxes the utmost skill of the chemist to effect even a partial separation, and their history is so obscure that we do not yet know the number of them.

It will not be necessary here to explain in detail the process of chemical fractionation adopted for the separation of the rarer earths, since it could interest only the chemical specialist; moreover, it has been fully described in a paper I read before the British Association at Birmingham.

Stated in the briefest way the operation consists in fixing upon some chemical reaction in which there is the most likelihood of a difference in the behaviour of the elements under treatment, even though the difference be slight, and effecting such treatment incompletely, so that only a certain fraction of the total bases present is separated; the object being to get part of the material in an insoluble and the remainder in a soluble state.

Let us suppose that we have in solution two earths almost identical in their properties, but differing slightly, almost imperceptibly, in basicity. We add to the solution of the earths, which must be very dilute, weak ammonia to such an amount only that it precipitates one-half of the bases present. The dilution must be so great that a considerable time must elapse before the liquid shows a turbidity, and several hours will have to pass over before the action of the ammonia is complete. The liquid is then filtered, by which process we have the earths divided into two parts, no longer identical in their composition. We can easily see that there is now a slight difference in the basic value of the two portions of earths; the portion in solution being, though by a scarcely perceptible amount, more basic than that which the ammonia has precipitated. This minute difference is made

* A Lecture delivered at the Royal Institution, on Friday Evening, February 18th, 1887.

to accumulate systematically until it becomes perceptible either by chemical or physical tests.

The accompanying diagram (Fig. 1) illustrates the scheme of fractionation. Starting from zero at the apex the precipitates all pass to the left and the filtrates to the right. Each circle represents a flask containing the solution under treatment, and the two arrows from each circle show the path pursued respectively by the precipitate and filtrate.

Such is the general outline of the process. But, as has been already intimated, the methods of separation suitable for different groups of earths vary. Where the constituents of yttrium and samarium are concerned, nothing seems available but straightforward fractionation continued month after month and year after year.

The further question whether an earth we have separated is really simple or is still a mixture has again to be decided by yet another process, to be effected only in a vey high vacuum. To understand this process it is necessary to make an apparent total digression.

It seems, perhaps, strange to speak of exhausting the air in hollow bulbs and tubes until there is left in them only the one-millionth part of an atmosphere. It is only in modern times that atmospheric air has come to be regarded as matter. To this day a bottle or a jar is said to be "empty" if it contains no liquid or solid body, the air with which it is filled being completely ignored. According to the same common idea, how empty then must a vessel be when the air it contains is reduced to the one-millionth part of its original quantity! That something still remains is, however, proved by the fact that I have succeeded in reducing the pressure down to one fifty-millionth of an atmosphere. What this number represents will be better understood if I say that, given a barometric column one hundred miles in height, the remaining pressure would be equal only to about the tenth of an inch. Even this high degree of exhaustion by no means represents an absolute vacuum. I have in this glass tube perhaps the nearest approach to perfect emptiness yet artificially obtained. Its internal capacity is 5 cubic centimetres, and it is exhausted to the one fifty-millionth part of an atmosphere. It still contains 100,000000,000000 molecules. The internal space, therefore, is far, very far, from being absolutely void of matter.

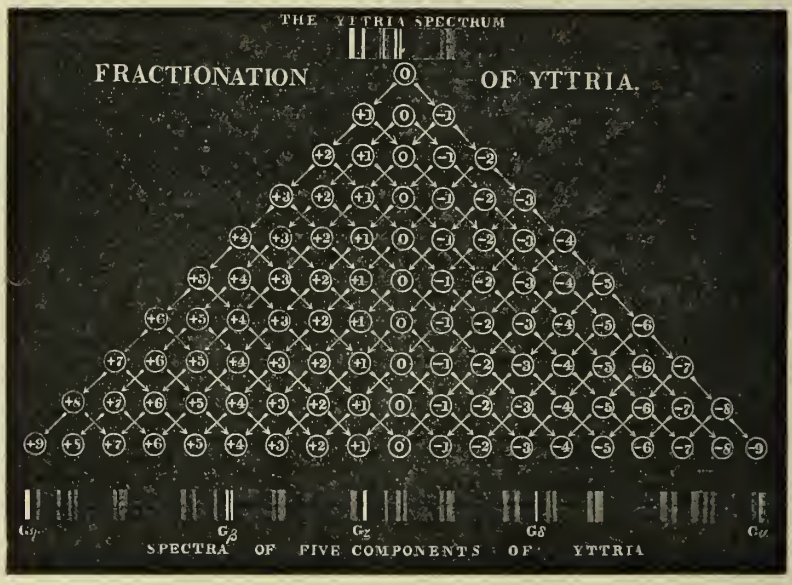
The vacuum most suitable for experiments on these earths is one of about the millionth of an atmosphere. In a vacuum of this degree we find under the action of the induction-spark certain substances phosphorescing or behaving very differently from what they would if similarly treated at a lower vacuum or at the ordinary pressure of the atmosphere. When thus treated, the examination of the spectra of the phosphorescing earths furnishes what I have ventured to call the radiant-matter test.

After a time, on examining the series of yttrium earths in the lowest line of flasks, their phosphorescent spectra are found to have become modified in the relative intensities of some of their lines. Ultimately different portions of the fractionated yttria give the five spectra approximately shown at the foot of the diagram; whilst samaria also appears capable of being split up into two or perhaps three constituents.

These bodies, it must be clearly understood, are not impurities which may be removed, yttrium or samarium remaining in a pure state after their elimination. On the contrary, the molecule we formerly knew as yttrium has undergone a veritable splitting up into its constituents.

These constituents I have not as yet formally baptized. For more convenient reference and discussion I have provisionally ticketed them, as shown in the accompanying Table. (See Table I., next page).

Fig. 1.




I will rapidly sketch the most salient features of the rare earths when submitted to the radiant-matter test. Some remain unaffected and thus are referred at once to a distinct group. Others have the curious property of preventing the induction-spark passing, and so simulating a non-conducting vacuum, when there is really plenty of residual gas present. The rare earth thoria possesses in the highest degree this obstructive property. Before me I have an exhausted tube having two sets of poles sealed in it, one set at each end. The size and distance apart of these poles are exactly the same in each case. At one end of the tube I have put some thorium sulphate, at the other end I have put yttrium sulphate. The exhaustion is now proceeding by aid of the Sprengel pump. I attach the wires of the induction coil to the poles at the thorium end, and, as you see, no current will pass: rather than pass through the tube, the spark prefers to strike across the spark-gauge in air,—a striking distance of 37 millimetres,—showing an electromotive force of 34,040 volts.

Table I.

| Position of lines in the spectrum. | Scale of spectroscope. | Mean wave-length of line or band. | $\frac{1}{\lambda^2}$ | Provisional name. | Probability. |
|---|---|---|---|---|---|
| Bright lines in— | | | | | |
| Violet .. .. .. .. | 8·515 | 456 | 4809 | Sγ | New, or ytterbium. |
| Deep blue.. .. .. .. | 8·931 | 482 | 4304 | Gα | New. |
| Greenish blue (mean of a close pair) .. .. .. | 9·650 | 545 | 3367 | Gβ | New, or the Zβ of M. de Boisbaudran. |
| Green .. .. .. .. | 9·812 | 564 | 3144 | Gγ | New. |
| Citron .. .. .. .. | 9·890 | 574 | 3035 | Gδ | New, or the Zα of M. de Boisbaudran. |
| Yellow .. .. .. .. | 10·050 | 597 | 2806 | Gε | New. |
| Orange .. .. .. .. | 10·129 | 609 | 2693 | Sδ | New. |
| Red .. .. .. .. .. | 10·185 | 619 | 2611 | Gζ | New. |
| Deep red .. .. .. .. | 10·338 | 647 | 2389 | Gη | New. |

Now, without doing anything to affect the degree of exhaustion, I transfer the wires of the induction coil from the thorium to the yttrium end, and the spark passes at once. To balance the spark in air I must push the wires of the gauge together, till they are only 7 millimetres apart, equivalent to an electromotive orce of 6440 volts; the fact of whether thoria or yttria is under the poles making a difference of 27,600 volts in the conductivity of the tube. The explanation of this eccentric action of thoria is not yet quite clear. From the great difference in the phosphorescence of the two earths, it is evident that the passage of electricity through these tubes is not so much dependent on the degree of exhaustion as upon the phosphorogenic property of the body opposite the poles.

Other earths become very phosphorescent, and their power of retaining residual phosphorescence differs greatly among themselves. This property we shall presently see is one of some importance. To examine this persistence of luminosity I have devised an instrument similar to Becquerel's phosphoroscope, but acting electrically instead of by means of direct light. It consists of an opaque disk, 30 inches in diameter, pierced with six openings near the edge. By means of a multiplying wheel and pulley the disk can be set in rapid rotation. At each revolution a stationary object behind one of the apertures is alternately exposed and hidden six times. A commutator forms part of the axis of the disk, and by connecting it with the wires from a battery, rotation of the disc produces alternate makes and breaks in the current. This primary current is then connected with the induction coil, from which the secondary current passes through the vacuum tube containing the earth under examination. When a phosphorescent body such as yttria is examined, if the wheel is turned slowly no light is seen when looked at from the front, as the current does not begin till the obscuration of the tube by an intercepting segment, and ends before the earth comes into view. When, however, the wheel is quickly turned, the residual phosphorescence lasts long enough to bridge over the brief interval between the cessation of the spark and the entry of the phosphorescent body into the field of view, and it is seen to glow with a faint light which becomes brighter as the speed of the wheel increases.

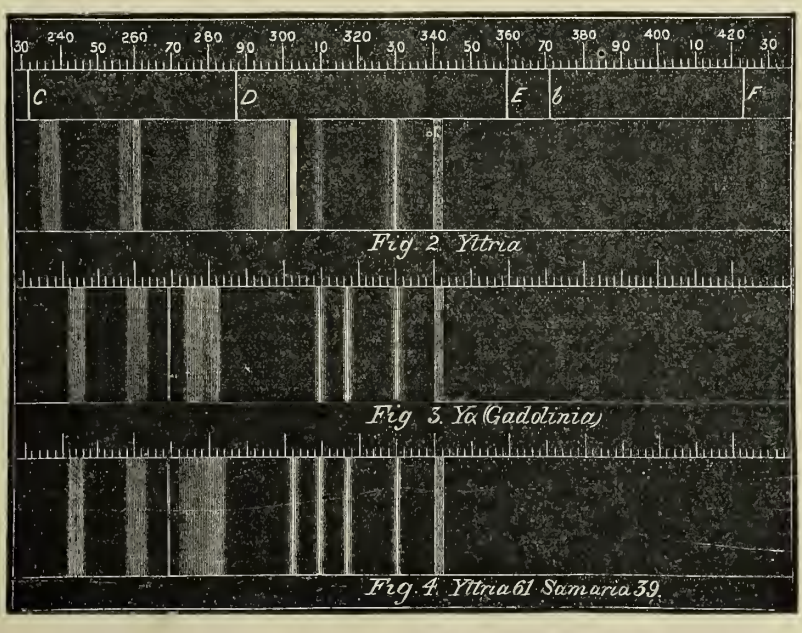


Fig. 2. Yttria

Fig. 3. Yα (Gadolinia)

Fig. 4. Yttria 61 Samaria 39

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I will first put the phosphorescent earth glucina in the phosphoroscope. This phosphoresces of a bright blue colour, but the residual glow is so short that, with the highest speed of which the instrument is capable, you see no light whatever. In contrast I now put in a compound of the earth strontia. This also glows with a rich blue colour, showing in the spectroscope a continuous spectrum with a great concentration of light in the blue and violet. In the phosphoroscope the colour of the glow is bright green, showing in the spectroscope a continuous spectrum, with the red and blue ends cut off.

Alumina in the radiant matter tube glows with a rich crimson light. I will put some rubies—a crystalline form of alumina—in the phosphoroscope. Here the persistence of luminosity is so great that the red light is visible with the slowest speed, and with a high velocity the residual glow is nearly as strong as when the rubies are out of the instrument. Shakspere, who is supposed to have

mastered all knowledge, had he seen these rubies could hardly have described them more precisely than in the lines from "Julius Cæsar":—

" . . . with unnumbered sparks
They are all fire, and every one doth shine."

Another distinctive phenomenon is that the earths of one group, yttrium and samarium, when submitted to the induction discharge *in vacuo*, yield discontinuous spectra.

These spectra are extremely complicated and change in their details in a puzzling manner. For many years I have persistently groped on in almost hopeless endeavour to get a clue to the meaning which I felt convinced was locked up in these systems of bands and lines. It was impossible to divest myself of the conviction that I was looking at a series of autograph inscriptions from the molecular world, evidently of intense interest, but written in a strange and baffling tongue. For a long time all attempts to decipher these mysterious signs were fruitless.

The meaning of the strongly-marked symbolic lines had first to be ascertained. After continued effort I had to be content with roughly translating one group of coloured symbols as "yttrium" and another group as "samarium," disregarding the fainter lines, shadows, and wings frequently common to both. Constant practice in the decipherment has now given me fuller insight into what I may call the grammar of these hieroglyphic inscriptions. Every line and shadow of a line, each faint wing attached to a strong band, and every variation in intensity of the shadows and wings among themselves, has now a definite meaning, which can be translated into the common symbolism of chemistry.

This leads us to what I may call the history of yttrium. Twelve months ago the name yttrium conveyed to all chemists a perfectly definite meaning. It was supposed to be an elementary or simple body, having a fixed atomic weight, 88·9, and its principal properties had been duly determined. Its phosphorescent spectrum gave a definite system of coloured bands, such as you see in the drawing before you (Fig. 2). Broadly speaking, there is a deep red band, a red band, a very luminous citron-coloured band, a pair of greenish-blue bands, and a blue band. These bands, it is true, varied slightly in relative intensities and in sharpness with almost every sample of yttria I examined; yet the general character of the spectrum remained unchanged, and I habitually looked upon this spectrum as characteristic of yttrium; all the bands being visible when the earth was present in quantity, whilst only the strongest of all—the citron band—was visible when traces, such as millionths, were present. But that the whole system of bands spelled yttrium, and nothing but yttrium, I was firmly convinced.

The differences in the spectra of yttrium prepared from different sources are most distinctly seen on comparing the spectrum of yttrium from samarskite with that from gadolinite, hielmite, monazite, xenotime, fluocerite, euxenite, cerite, arrhenite, &c. Still, in spite of these slight differences, the several yttriums are practically all the same thing, and, as I have said, every living chemist a year ago would have regarded them as identical. But they have since yielded to persistent chemical fractionation, and I now call them old yttrium.

One property, above all others, is relied on by chemists as an indisputable proof of the identity of any particular chemical element. When the vapour of an element is rendered incandescent by the electric spark, the characteristic system of lines in its spectrum is regarded as unalterable, and is looked upon as a certain proof that this special element is under examination. However much chemical or other tests fail to show the presence of a given element, the indications of its lines in the spectroscope are regarded as infallible. Spectrum analysis is the court of final appeal, whose decision no chemist has yet had the hardihood to dispute.

By way of illustration I will project on the screen the very characteristic system of lines given by yttrium when ignited by the electric spark,—a system, be it remembered, having no connection whatever, with the peculiar phosphorescent spectrum yielded by yttrium. The coloured diagram gives as accurate a representation of the spark spectrum of yttrium as can be drawn by hand. Omitting minor lines you will notice two very strong groups of lines in the red and orange. These lines have been always regarded as the characteristic test for yttrium; the presence of these groups proves the presence of yttrium, and their absence proves its absence.

I now project the electric spark spectrum of Gδ, as pure as I have been able to prepare it. Gδ is one of the bodies which by long and tedious fractionation I have separated from yttrium; it occurs at one extreme end of the fractioning, and differs not only from the parent yttrium in its phosphorescent spectrum, but by virtue of the process adopted for its isolation it must likewise differ in chemical properties. But what tale does the spectrum tell? It tells us there is absolutely no difference between this spectrum and that given by old yttrium.

I now pass to the other end of the fractionation of yttrium, where a body, Gη, concentrates giving a totally different phosphorescent spectrum to that given by Gδ. And it also differs chemically from old yttrium, and in a more marked manner from its brother, Gδ, at the other extremity of the fractionation. Look at its spark spectrum! It is perfectly identical both with old yttrium and with Gδ, and when I examine these three spectra in my laboratory with all the appliances for exact measurement, the whole system of lines is still identical.

What inference can be drawn from these results? Is discredit to be thrown on spectrum analysis? Is the superstructure which has been so laboriously raised upon its indications to fall to the ground? By no means. Spectrum analysis and its grand generalisations are on as firm a foundation as ever. I see two possible explanations of the facts I have brought before you. According to one hypothesis research has somewhat enlarged the field lying between the indications given by ordinary coarse chemistry and the searching scrutiny of the prism. Our notions of a chemical element have expanded. Hitherto the molecule has been regarded as an aggregate of two or more atoms, and no account has been taken of the architectural design on which these atoms have been joined. We may consider that the structure of a chemical element is more complicated than has hitherto been supposed. Between the molecules we are accustomed to deal with in chemical reactions and ultimate atoms as first created, come smaller molecules or aggregates of physical atoms; these sub-molecules differ one from the other, according to the position they occupied in the yttrium edifice.

Perhaps this hypothesis can be simplified if we imagine yttrium to be represented by a five-shilling piece. By chemical fractionation I have divided it into five separate shillings, and find that these shillings are not counterparts, but like the carbon atoms in the benzol ring, have the impress of their position, 1, 2, 3, 4, 5, stamped on them. These are the analogues of my Gα, Gβ, &c. If I now bring in a much more powerful and searching agent,—if I throw my shillings into the melting-pot or dissolve them chemically,—the mint stamp disappears and they all turn out to be silver. I submit my yttrium, or my Gα, Gβ, &c., to the intense heat of the electric spark, the little differences of molecular arrangement vanish, and the atoms, of which the molecules of yttrium, Gα and Gβ are alike composed reveal their presence in identical spectra.

An alternative theory commends itself to chemists, to the effect that the nine bodies shown in the above table (Table I), are new chemical elements differing from yttrium and samarium in basic powers and several other chemical and physical properties, but not sufficiently to enable us to effect any but a slight separation. One of these bodies, Gδ, gives the phosphorescent citron line, and also the brilliant electric spectrum I have just exhibited. The other eight do not give electric spectra

which can be recognised in the presence of a small quantity of Gδ, whilst the electric spectrum of Gδ is so sensitive that it shines out in undiminished brilliancy even when the quantity present is extremely minute. In the process of fractionation, Gα, Gβ, Gδ, &c., are spread out and more or less separated from one another, yet the separation is imperfect at the best, and at any part there is enough Gδ to reveal its presence by the sensitive electric spark test. The arguments in favour of each theory are strong and pretty evenly balanced. The compound molecule explanation is a good working hypothesis, which I think may account for the facts, while it does not postulate the rather heroic alternative of calling into existence eight or nine new elements to explain the phenomena. However, I submit it only as an hypothesis. If further research shows the new element theory is more reasonable, I shall be the first person to accept it.*

I now will introduce to you a substance which has been to me what the celebrated Rosetta stone was to the interpreters of Egyptian inscriptions. I received it from M. de Marignac, and it was nothing more than a small specimen of a new earth which he had obtained and had named provisionally Yα.

In the radiant-matter tube this earth gives a bright spectrum as in the diagram before you (Fig. 3).

If we compare this spectrum with that ascribed to "old yttrium" (Fig. 2) we see that, omitting minor details, Yα is yttrium with the characteristic citron band left out and the green and orange bands of samarium added. Now look at the following diagram (Fig. 4), which represents the spectrum of a mixture of 61 parts of yttrium and 39 parts of samarium. It is almost to its minutest details identical with the spectrum of Yα, but the citron band is as prominent as any other band. Hence Yα is shown to consist of samarium, with the greenish blue of yttrium and some of the other yttrium bands added to it. It proves, further, that the citron band which I had hitherto regarded as one of the essential bands of the yttrium spectrum can be entirely removed, whilst another characteristic yttrium group, the double green band, can remain with heightened brilliancy.

If now it were possible to remove the citron band-forming body from this mixture, I should leave Yα behind; I should, in fact, have recomposed Yα from its elements. I have no doubt whatever that this will ultimately be accomplished, but the preliminary work of fractionation is tedious to the last degree, and for its completion would occupy a space of time in comparison with which the life of man is all too brief.

Whilst I have not yet chemically removed the citron forming constituent, I can physically suppress the citron band and show an artificial spectrum, imitating in the closest degree the natural spectrum of Yα.

By means of the electrical phosphoroscope I am enabled to catch the spectrum of an earth immediately after it has suffered molecular bombardment in the vacuum. In this way I get the spectrum of the residual phosphorescence, and I have found that not all the constituents of these earths emit residual phosphorescence for the same duration of time.

When a little strontium is added to the yttrium-samarium mixture, the effect in the phosphoroscope is to suppress the residual phosphorescence of Gδ—the citron band—and to enhance the phosphorescence of Gβ, the double green band, and the imitation of the Yα spectrum is complete.

I must here call attention to the experiments of Prof. A. E. Nordenskiöld, in the *Comptes Rendus* of the French Academy of Sciences for November 2nd, 1886. This eminent savant is working in the same direction as myself, with results which decidedly corroborate my experiments. He has taken the crude mixture of yttria, erbia, ytterbia, &c., just as it is precipitated from the minerals containing these rare earths. This mixture, for brevity's sake, he calls gadolinia, and he finds that this gadolinia, though palpably a compound body, has always a constant atomic weight, whatever the mineral from which it has been extracted. Or, to use Prof. Nordenskiöld's own words, "*Oxide of gadolinium, though it is not the oxide of a simple body, but a mixture of three isomorphous oxides* (even when it is derived from totally different minerals found in localities far apart from each other) *possesses a constant atomic weight.*" Therefore, as he significantly observes, "*We are in presence of a fact altogether new in chemistry.* For the first time we are confronted with the fact that three isomorphous substances, of a kind that chemists are still compelled to regard as elements, occur in nature not only always together, but in the same proportions. It seems that chemists here find themselves face to face with a problem analogous to that presented to astronomers in the origin of the minor planets."

These facts throw a new light upon certain important chemical questions. For the old yttrium passed muster as an element. It had a definite atomic weight, it entered into combination with other elements, and could be again separated from them as a whole. But now we find that excessive and systematic fractionation has acted the part of a chemical "sorting Demon," distributing the atoms of yttrium into groups, with certainly different phosphorescent spectra, and presumably different atomic weights, though, from the usual chemical point of view, all these groups behave alike. Here, then, is a so-called element whose spectrum does not emanate equally from all its atoms; but some atoms furnish some, other atoms others, of the lines and bands of the compound spectrum of the element. Hence the atoms of this element differ probably in weight, and certainly in the internal motions they undergo.

This is unlikely to be an isolated case. We may assume that the principle is of general application to all the elements. In some, possibly in all elements, the whole spectrum does not emanate from all their atoms, but different spectral rays may come from different atoms, and in the spectrum as we see it all these partial spectra are present together. This may be interpreted to mean that there are definite differences in the internal motions of the several groups of which the atoms of a chemical element consist. For example, we must now be prepared for some such events as that the seven series of bands in the absorption-spectrum of iodine may prove not all to emanate from every molecule, but that some of these molecules emit some of these series, others others, and in the jumble of all these molecules, to which is given the name "iodine vapour," the whole seven series are contributors.

Another important inference to be drawn from the facts is that yttrium atoms, though differing, do not differ continuously, but *per saltum*. We have evidence of this in the fact that the spectroscopic bands characteristic of each group are distinct from those of other groups, and do not pass gradually into them. We must accordingly expect, in the present state of science, that this is probably the case with the other elements. And the atoms of a chemical element being known to differ in one respect may differ in other respects, and presumably do somewhat differ in mass.

Returning, after this digression, to the idea of heavy

* Neither of these theories agrees with that of my distinguished friend, M. Lecoq de Boisbaudran, who also has worked on these earths for some time. He considers that what I have called old yttrium is a true element, characterised by the spark spectrum already exhibited, but not giving a phosphorescent spectrum *in vacuo*. The bodies giving the phosphorescent spectra he considers to be impurities in yttrium. These he says are two in number, and he has provisionally named them Zα and Zβ. By a method of his own, differing from mine, M. de Boisbaudran obtains fluorescent spectra of these bodies; but their fluorescent bands are extremely hazy and faint, rendering identification difficult. Some of them fall near lines in the spectra of my Gβ and Gδ. At first sight it might appear that his and my spectra were due to the same bodies, but, according to M. de Boisbaudran, the chemical properties of the earths producing them are widely distinct. Those giving phosphorescent lines by my method occur at the yttrium extremity of the fractionation, where his fluorescent bands are scarcely shown at all; whilst his fluorescent phenomena are at their maximum quite at the terbium end of the fractionation, where no yttrium can be detected even by the direct spark, and where my phosphorescent lines are almost absent.

and light atoms, we see how well this hypothesis accords with the new facts here brought to light. From every chemical point of view the stable molecular group, yttrium, behaves as an element. To split up yttrium requires not only enormous time and material, but the existence of a test by means of which the constituents of yttrium are capable of recognition. Had we tests as delicate for the constituent molecular groups of calcium, this element also might be resolved into simpler groupings. It is one thing, however, to find out means of separating bodies which we know to be distinct and to have colour or spectrum reactions to guide us at every step; it is quite another thing to separate colourless bodies which are almost identical both in chemical reaction and atomic weight, especially if we have no suspicion that the body we examine is a mixture.

Again it seems as if bodies we have been accustomed to regard as absolutely simple and elementary may be split up in different directions according to the means we bring to bear upon them. Until very lately our text-books made mention of an element under the name of didymium. With some trouble it had been separated from its accompanying bodies lanthanum and cerium. Its properties had been examined, and no one doubted its distinct and elementary character. It was viewed according to one of the common definitions of an element, as "a something to which we can add, but from which we can take nothing." When, behold! Dr. Auer von Welsbach, examining this supposed simple body in a novel manner, succeeded in decomposing it into two simpler bodies, which he called neodymium and praseodymium; and later researches, in which I have had a share, show that even neodymium and praseodymium are not the simplest bodies into which didymium can be dissected.

(To be continued.)

## A NEW APPARATUS FOR THE DETERMINATION OF VAPOUR DENSITIES.

By Dr. GIBSON DYSON.

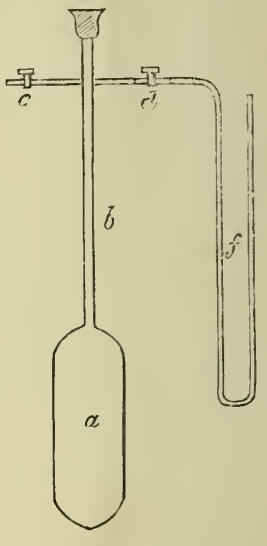
I HAVE for some time past been engaged with the construction of a new apparatus for the determination of vapour densities of such substances as are not volatile without decomposition in contact with air or under ordinary atmospheric pressure. So far I have every reason to believe the process to be trustworthy, and I hope before long to publish a series of determinations bearing out this view. Unfortunately, circumstances compel me to publish the work in this incomplete form.

It is proposed to determine the vapour densities of solid and liquid substances by measuring the increase of pressure caused by the volatilisation of a known weight of the substance in a given space. The apparatus employed is represented in the adjoining figure. *a* is a bulb of about 250 c.c. capacity, and to this is attached a tube (*b*) having an inner diameter of 4—5 millimetres and a length of 5 decimetres. This tube is widened at the top to admit of an arrangement, similar to that used with V. Meyer's apparatus, so that the substance can be introduced without removing the cork. To the tube *b* are fused two capillary side tubes, *c* and *d*, each of which is fitted with a stop-cock. The tube *d* is connected with the manometer, *f*. The capacity of the bulb *a* and tube *b* must now be ascertained, and the apparatus is then ready for use.

The following is the manner in which a determination is conducted:—

The apparatus is first thoroughly dried by passing a current of dry air through it, and then some dry sand or asbestos is placed at the bottom of *a*. The bulb is next immersed in a bath, the temperature of which is known, and the weighed substance (about 0·05—0·1 grm.) is placed ready for dropping into the apparatus (one of the best arrangements for this purpose is that devised by L. Meyer, *B.*, 13, 991). If it is desired to conduct the experiment under reduced pressure, the tube *c* is connected with a mercury pump; as soon as the pressure in the apparatus is sufficiently reduced, the stop-cock at *c* is closed and the pump disconnected.

The heating is now continued until the temperature, and consequently the pressure, is constant, and then the substance is introduced. The pressure in the apparatus quickly rises, and as soon as it has reached its maximum the stop-cock at *d* is closed and that at *c* opened.




The increased pressure is now accurately read off on the manometer, and from this the vapour density of the substance can be calculated. If it is desired to conduct the experiment in an atmosphere of nitrogen, or any other gas, it is only necessary to displace the air in the apparatus by it before proceeding with the determination.

The following data are required:—

V = capacity of $(a)+(b)$.
$p$ = pressure before introduction of substance.
$p'$ = pressure after introduction of substance.
$t$ = temperature of bath.
S = weight of substance taken.

The vapour density is obtained by the following equation:—

$$\frac{S \times 760\,(1 + 0{\cdot}003665\,t)}{V \times (p' - p) \times 0{\cdot}001293} = \text{Vapour density.}$$

The Brooklyn Academy of Science.—This Academy has been recently formed with the object of affording an opportunity of scientific study and research to those who would otherwise be without. A course of free lectures is also being delivered on such subjects as "The Chemistry of Salt," "The Story of a Plant," &c. The Academy is under the supervision of Prof. G. W. Thompson.

Missouri School of Mines.—It having been found that the space allotted to chemical and metallurgical work at this school was inadequate, it was decided to apply to the Legislature for a new chemical laboratory. A grant having been made, plans were made by Prof. C. E. Wait, under whose supervision it was erected; and the school may now be congratulated on having a very commodious and well appointed laboratory, comprising two large rooms, one for qualitative and one for quantitative work, an assay laboratory, a large lecture theatre, two balance rooms, and two evaporating rooms.

# AN IMPROVEMENT IN THE PRODUCTION OF SULPHURIC ACID.

By H. SPRENGEL, Dr. phil., F.R.S.

Mechanical operations, such as the pumping of water and the compressing of air, absorb in Sulphuric Acid Works which possess Gay-Lussac- and Glover-towers a not inconsiderable amount of steam, and consequently of fuel. This steam, after having spent its energy in the engines, is (as a rule) allowed to escape into the open air. It is obvious that this escaping steam, the so-called "exhaust-steam," might render a second service by virtue of its chemical properties, if it could be made to substitute *(without much trouble and expense, and without causing irregularities and disorder)* a part of another quantity of steam, which in Sulphuric Acid Works has to be raised almost entirely for the sake of a chemical operation, viz., the formation of acid inside the leaden chambers.

This problem* I have solved in the following manner:†—

Be it remembered that the work done by a steam-engine is the result of the difference of pressure which exists alternately on the two sides of its piston. Supposing this pressure be 30 lbs. per square inch on the one side and *nil* on the other, the work done will be due to the difference of these 30 lbs. per square inch. Hence the same work may be done by the same engine, if the pressure be kept at 40 lbs. per square inch on the one side of its piston and at 10 lbs. per square inch on the other, for the difference of pressure remains unaltered, or 30 lbs. per square inch.

In factories of an average size not more than one steam-boiler serves, as a rule, to supply steam of a uniform pressure of about 30 lbs. per square inch both to the engines and to the chambers. As, however, a pressure of 10 lbs. per square inch is ample and to spare for the steam entering the chambers, I now, in harmony with the above view,—

(1) Raise the pressure in such a steam-boiler by 10 lbs. per square inch, *i.e.*, in this case from 30 lbs. to 40 lbs.,

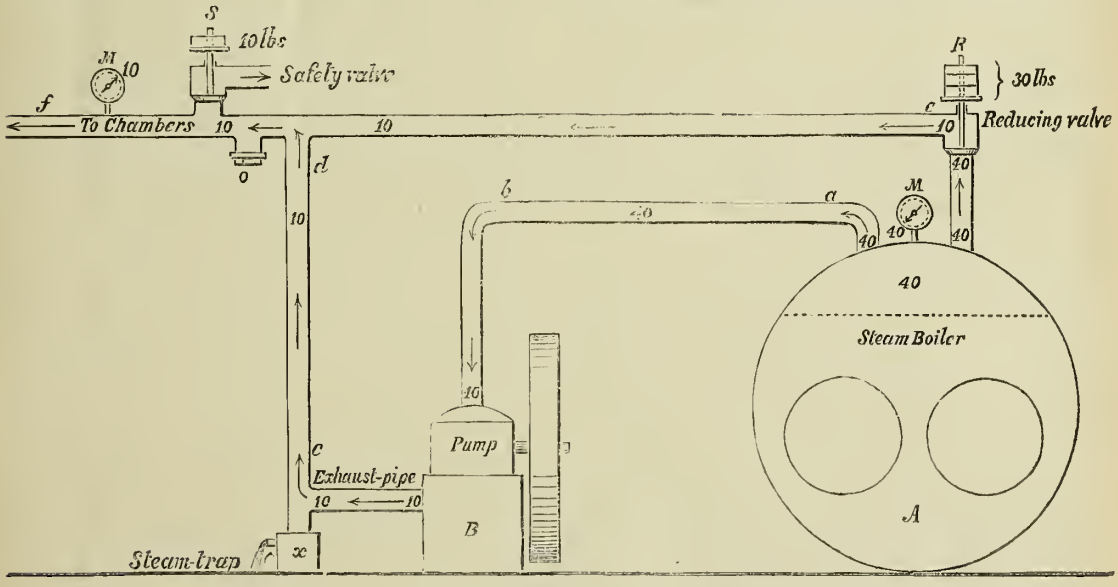
(2) Drive the engines at this higher pressure,

(3) Make the exhaust-steam from the engines enter the chambers at a pressure of 10 lbs. per square inch and—

(4) Supplement, when needed, any deficiency of steam in the chambers by another quantity of steam of the same pressure, *i.e.*, steam of 10 lbs. per square inch, drawn from this very boiler which is kept at a constant and regular pressure of 40 lbs. per square inch.

How this may be done, in a convenient and inexpensive manner, will be readily understood by referring to the annexed diagrammatic sketch.

A represents a steam-boiler and B a pump, supplied with steam of a constant pressure of 40 lbs. per square inch by the pipe *a b*. The exhaust-steam of this pump escapes through *c d* into the main steam-pipe *e f*, which carries steam of a pressure of 10 lbs. per square inch to the chambers. This main steam-pipe *e f* is connected with the steam-boiler A, and is provided with two valves:—




(1) A reducing-valve, R, and

(2) A safety- or escape-valve, S.

These two valves are weighted in such a manner that, as soon as the pressure in *e f* becomes less than 10 lbs. per square inch, the valve R will admit steam from the boiler until a pressure of 10 lbs. is re-established in *e f*; while as soon as the pressure in *e f* becomes more than 10 lbs. per square inch, the valve S will allow an escape of steam into the open air until a pressure of 10 lbs. is re-established in *e f*. In other words, and by way of an example, a 40 lbs. pressure in the boiler will lift and overcome a 30-lb. weight plus a 9½-lb. counter-pressure of steam at R, while a 10½-lb. pressure in *e f* will lift a 10-lb. weight at S.

Thus it will be seen that one boiler and one system of pipes are sufficient to supply simultaneously both the engines with high-pressure steam and the chambers with low-pressure steam.

To ensure, what is much to be desired, an even, constant, and regular pressure in *e f*, it is essential that these valves R and S should be sensitive, or, in technical language, not be liable to "stick."

M and M¹ represent manometers for indicating the pressure inside the boiler A and the pipe *e f*; while *x* represents a steam-trap and an outlet for condensed steam which in the form of water will collect in the pipes above *x*.

* For an attempt to solve this problem in a different manner by the help of *two* steam-boilers, and in a case where the exhaust steam was derived from *one engine only*, see Dr. G. Lunge's excellent "Treatise on the Manufacture of Sulphuric Acid and Alkali." London: Van Voorst. 1879, vol. i., pp. 393 and 565.

† The author's British patent No. 10,798 of Aug. 24, 1886.

In the same way as the exhaust-steam from only one pump is shown here to be utilised, so the exhaust-steam from two or more pumps may be utilised by connecting the same with *e f*, for instance at *o*.

Though this invention relates in the first instance to the utilisation of exhaust-steam of engines which are to be met with in every Sulphuric Acid Works possessing Gay-Lussac- and Glover-towers, it is obvious that the exhaust-steam from any other engine, which happens to be discharged into the open air in the vicinity of sulphuric acid chambers, may be utilised as before described, even if this exhaust-steam should be derived from an engine supplied with steam from a different boiler at a different pressure, for the regularity of pressure needed in the chamber steam-pipes will thereby not be affected, but will still be maintained by the valves R and S. In fact, the use of exhaust steam in the manufacture of sulphuric acid may be carried with advantage to the point at which the sum total of the thus collected quantity of exhaust-steam equals the total quantity of steam needed in the chambers.

Hence, only after this point has been passed, is there good reason to employ, in the vicinity of sulphuric acid chambers, engines from which there is no escape of exhaust-steam properly speaking, *e.g.*, the so-called condensing-engines.

Finally, I beg to state that I do not restrict myself to the above-stated pressures of 40 and 10 lbs. per square inch as the only ones which may be used. I merely have given these pressures as those at which I have obtained very satisfactory results.

As an experimental proof it may be mentioned that, by utilising in this manner the exhaust-steam from *four* small engines attached to the water-pumps and air-compressers at the Works of my licensees—the *Lawes' Chemical Manure Company*, Creek's Mouth, Barking, Essex—I have been able to dispense with one of two steam-boilers formerly in use, thus reducing the consumption of coal 34 per cent; the quality of coal and the amount of work done remaining unaltered. The savings in coal alone, at a price of 9s. 3d. per ton, repaid, in this instance, the cost of the apparatus after having been in use for three months and eight days, while the profit on the investment amounted to 370 per cent per annum. This apparatus has now been in daily use for one and a half years, delivering the steam, however varying and intermittent at its sources, with unfailing regularity and constancy of pressure at the chambers. It hardly need be said that this *regularity* and *constancy of pressure* is one of the factors on which a good yield of acid depends in no small a measure.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, February 17th, 1887.*

Dr. Hugo Müller, F.R.S., President, in the Chair.

Messrs. E. Hori and Charles E. Sohn, Jun., were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Harold Govett Colman, Owens College, Manchester; James Tudor Cundall, Dale Side, Hampton Redland, Bristol; Alfred John Evans, B.A., Sheegorah House, Boyle, Ireland; Arthur Harden, Ashville, Upper Charlton Road, Manchester; William Houlding, Stanley House, Anfield, Liverpool; Theophilus Horne Redwood, 154, Ladbroke Grove Road, W.; George Robertson, Madeira Villa, Woodford, Essex; W. Harry Stanger, 23, Queen Anne's Gate; Patrick T. O'Sullivan, 57, Great Britain Street, Cork.

It was announced that the following changes in the Council List were proposed by the Council:—

*As President*—Mr. W. Crookes, F.R.S., *vice* Dr. Hugo Müller, F.R.S.

*As Vice-Presidents*—Prof. M'Leod, F.R.S., Prof. Schorlemmer, F.R.S., and Mr. Ludwig Mond, *vice* Mr. Crookes, F.R.S., Prof. Liveing, F.R.S., and Prof. T. E. Thorpe, F.R.S.

*As Ordinary Members of the Council*—Prof. A. H. Church, Dr. P. F. Frankland, Prof. Kinch, and Dr. H. F. Morley, *vice* Messrs. H. T. Brown, A. E. Fletcher, and Profs. Meldola and Pickering.

Messrs. C. W. Heaton, P. F. Frankland, and Wyndham Dunstan were appointed by the meeting to audit the Treasurer's accounts.

The following papers were read:—

11. "*The Influence of Temperature on the Heat of Dissolution of Salts.*" By S. U. Pickering.

This is an extension of the author's previous work on the sulphates, entitled "The Influence of Temperature on the Heat of Chemical Combination" (*Trans.*, 1886, 260), which tended to show that the heat of dissolution of a salt does not increase regularly with a rise of temperature, but that irregularities occur at various points, so that the heat of dissolution must be represented by a series of curves. The experiments with potassium sulphate, hydrated and anhydrous magnesium sulphate, and hydrated and anhydrous copper sulphate have been repeated, and the investigation extended to potassium, sodium, hydrated and anhydrous strontium chloride, potassium and the two strontium nitrates, the two sodium carbonates, sodium acetate, and potassium sodium tartrates. The investigation comprises over 700 determinations, the mean results with each salt being deduced from two to five distinct series of experiments, each performed with different thermometers. The observations extended from 3° to 25°. In all cases it was found that the irregularities previously noticed were the result of error, and that the heat of dissolution of a salt is represented by a series of straight lines. In rising from low temperatures the heat of dissolution is expressed by a straight line up to a certain point, when the rate becomes suddenly lowered, and remains constant till a further sudden reduction occurs at some still higher temperature. The average divergence of all the mean results from lines of perfect straightness amounted to less than one-thousandth of a degree.

With the normally anhydrous salts one lowering of the rate (amounting to about 30 per cent) only was observed between 3° and 25°, occurring at temperatures between 14° and 9·5° in the various cases; while with the salts which combined with water of crystallisation the first alteration occurred at temperatures between 9° and 7°, and a second change took place at 21° to 18°; the frequency as well as the temperature of occurrence appearing to depend mainly on the tendency of the salt to combine with water. This lowering of the rate of increase in the heat of dissolution as the temperature rises must be accompanied by an increase in the specific heat of the solution which would indicate decomposition of some description.

Marignac's determinations of the specific heat of solutions give a rate of increase agreeing very closely with the author's results, and they also show that a further lowering takes place at temperatures above 25° up to 50°. Tilden's direct determinations of this rate at the higher temperatures show a very much larger decrease in the rate, but they cannot be freely accepted, as they are entirely at variance not only with all specific heat determinations, but also with a fundamental principle of thermo-chemistry.

The heat of combination of a salt with its water of crystallisation is deduced from the author's results. He concludes that it is not a constant quantity at all temperatures, the general effect of rise of temperature being to

diminish it, although at very low temperatures this effect seems to be more than counterbalanced by some other cause, probably the tendency of the water molecules to unite with each other, the heat of combination diminishing then with fall of temperature. The more water a salt contains the more marked are both these results.

DISCUSSION.

Dr. ALDER WRIGHT thought that the Society was to be congratulated on the fact that one of its members had undertaken the laborious and delicate work involved in making accurate thermo-chemical determinations of heats of dissolution, and in avoiding the numerous sources of error which attend such valuations. He found it somewhat difficult to realise the practicability of obtaining exactitude of such an order that the experimental errors should not exceed two or three calories, which apparently Prof. Pickering claimed to have done. Julius Thomsen, in his most accurate and painstaking researches, generally found a minimum variation from the mean in consecutive observations of from $\pm 5$ to $\pm 10$ calories; and Dr. Alder Wright himself, whilst working on the heat of dilution of concentrated solutions (with, however, less complete appliances than those used by Thomsen), found that about $\pm 10$ calories was the minimum experimental error attaching to each separate valuation. The question of the amount of the experimental error seriously affected Prof. Pickering's conclusion, that the curves indicating his results frequently consisted of two or more straight lines, making an angle or sudden break in the curve; it would seem far more probable, *à priori*, and in view of the general course of physical phenomena, in which some value is a function of the temperature, that the curve is truly *a curve* throughout, expressible by some such symbols as $1+at+\beta t^2$, where $\beta$ may be + or −. Judging from some of Prof. Pickering's diagrams, the deviations exhibited by some of his observations from the sets of straight lines deduced by him as mean results, are as great as, if not greater than, the deviations which they would exhibit from a mean curve of this kind; and until it had been shown that the deviations in this latter case were materially wider than could be accounted for by the degree of magnitude of the experimental errors, whilst in the former case this was not so (which so far Prof. Pickering had not done), he should feel some degree of difficulty in accepting the conclusion that the curves are not regular ones, but are portions of the bounding circumferences of irregular polygons.

[Prof. TILDEN writes, with reference to the statement made by Mr. Pickering, that he had used too little water in his experiments on the heat of dissolution of potassium sulphate, and that the salt could not have been all dissolved, that in every experiment of which the results were quoted in his paper the salt was entirely dissolved.]

12. "*Periodates.*" By C. W. KIMMINS, D.Sc., B.A. (Contribution No. IX. from the Laboratory of Gonville and Caius College, Cambridge).

The author, at the suggestion of Mr. Pattison Muir, has re-examined certain periodates of potassium, silver, and sodium, with the object of explaining the discordant results of various observers.

Besides the salt, $Na_2H_3IO_6$, described by Langlois, he has obtained a sodium periodate of the formula $Na_3H_2IO_6$; he also describes a potassium periodate, $K_3HI_2O_9$. He has prepared and analysed the following silver salts:—

| | |
|---|---|
| $Ag_2HIO_5$, dark brown. | $AgIO_4$, bright yellow, |
| $Ag_2H_3IO_6$, dark red. | $Ag_4I_2O_9{\cdot}3OH_2$, light yellow. |
| $Ag_3H_2IO_6$, slate-coloured. | $Ag_4I_2O_9{\cdot}OH_2$, claret-col'd. |
| $AgIO_4{\cdot}OH_2$, orange. | $Ag_4I_2O_9$, chocolate-coloured. |

13. "*Sulphonic Acids derived from the β-Monohaloid-derivatives of Naphthalene.*" By HENRY E. ARMSTRONG and W. P. WYNNE, B.Sc.

Experiment having shown that the sulphonic acids obtained from napthalene under conditions by which the occurrence of secondary change—which undoubtedly takes place when sulphuric acid is used as a sulphonating agent—is avoided, differ from those formed by means of sulphuric acid; and that the α-monohaloid derivatives of naphthalene yield isomeric sulphonic acids: it became desirable to study the behaviour of the β-monohaloid-derivatives.

By the action of fuming sulphuric acid at 130° to 140° on β-chloronaphthalene, Arnell (*Bull. Soc. Chim.*, xlv., 184) has obtained two isomeric acids: one of these yields a sulphochloride melting at 129°, which is converted into δ-dichloronaphthalene by distillation with $PCl_5$; the sulphochloride of the isomeride melts at 109°, and yields ε-dichloronaphthalene.

By acting with $SO_3HCl$ on β-chloronaphthalene in molecular proportions, the authors have also obtained two isomeric acids, which are undoubtedly identical with those discovered by Arnell. The *barium* salt of the chief product, $(C_{10}H_6Cl{\cdot}SO_3)_2Ba{\cdot}4H_2O$, crystallises in laminæ; the *potassium* salt, $C_{10}H_6Cl{\cdot}SO_3K+H_2O$, crystallises in small scales. The isomeric salts, $(C_{10}H_6Cl{\cdot}SO_3)_2Ba$ and $C_{10}H_6Cl{\cdot}SO_3K{\cdot}\frac{1}{2}H_2O$, are much less soluble in water.

β-Bromonaphthalene, in like manner, yields two isomeric acids. The *barium* salt of the chief product, $[C_{10}H_6Br{\cdot}SO_3]_2Ba{\cdot}3\frac{1}{2}H_2O$, and the *potassium* salt,—

$$C_{10}H_6Br{\cdot}SO_3K{\cdot}1\tfrac{1}{2}H_2O,$$

crystallise in thin octagonal scales. The corresponding salts of the isomeric acid are anhydrous and very sparingly soluble in water; the barium salt crystallises in tufts of flat needles, the potassium salt in thin lustrous laminæ.

β-Iodonaphthalene also yields two isomeric acids. The barium salt of the chief product. $[C_{10}H_6I{\cdot}SO_3]_2Ba{\cdot}4\frac{1}{2}H_2O$, and the potassium salt, $C_{10}H_6I{\cdot}SO_3K{\cdot}H_2O$, crystallise in thin hexagonal scales. The salts of the isomeric acid are very sparingly soluble in water; the lead salt,—

$$[C_{10}H_6I{\cdot}SO_3]_2Pb{\cdot}2\tfrac{1}{2}H_2O,$$

crystallises in scales: the barium salt,—

$$[C_{10}H_6I{\cdot}SO_3]_2Ba{\cdot}2H_2O,$$

in white flat needles; and the potassium salt,—

$$C_{10}H_6I{\cdot}SO_3K{\cdot}H_2O,$$

in well-defined laminæ.

Inasmuch as the action takes place between theoretical quantities of the reacting bodies, there can be little doubt that the products result from primary changes: a very small proportion, however—at most 3 or 4 per cent—of the haloid compound, is converted into the acid yielding the less soluble salts. Assuming, as is probable, that the products from chloro-, bromo-, and iodonaphthalene correspond in composition, the proof of the production of ε-derivatives in this manner is of considerable theoretical importance: although not absolutely placed beyond doubt, there is every reason to believe that ε-dichloronaphthalene is the *symmetrical heteronucleal* $\beta_2\beta_3'$-derivative; and the formation of such derivatives affords a clear indication of the existence of what one of the authors has termed a plane of symmetry in the naphthalene molecule, corresponding to a diagonal passing through two β-positions in the two nuclei of the naphthalene symbol, a more convincing proof of which perhaps is afforded by the complete conversion of β-naphthyl sulphate on heating at 100° into β-naphthol-β-sulphonic acid, which is also an ε-di-derivative (*Ber.*, xv., 203).

14. "*The Decomposition of Potassium Chlorate and Perchlorate by Heat.*" By FRANK L. TEED, D.Sc.

The results published in the paper on this subject by Dr. P. F. Frankland and Mr. J. Dingwall in *Proc. Chem. Soc.*, No. 32, as far as they go, entirely confirm certain results obtained by me, and announced in two papers, abstracts of which appeared in *Proc. Chem. Soc.*, Nos. 12 and 16 of the Session 1885 86.

In my latter paper I say that when the salt is very gently heated the decomposition more nearly approximates to the equation $22KClO_3 = 14KClO_4 + 8KCl + 5O_2$, to which Frankland and Dingwall make no reference, the majority

of the results falling within the limits of this equation and of the equation $10KClO_3 = 6KClO_4 + 4KCl + 3O_2$. On adding these two equations together and reducing to the lowest terms, the Frankland-Dingwall equation is obtained, which is merely one of the many equations that could be formed to express intermediate stages of decomposition.

There seems to be an idea among certain chemists that the determination of the evolved oxygen and of the potassium chloride are insufficient data from which to construct an equation, and that it is necessary to directly determine the perchlorate formed; or at all events, the undecomposed chlorate. This idea is erroneous, because it is obvious that for every 74·5 parts of KCl formed there must have been 122·5 of $KClO_3$ decomposed; and of the resulting 48 parts of oxygen, what is not evolved in the free state *must* have gone to form perchlorate. Any determinations of the $KClO_3$ and $KClO_4$ are therefore unnecessary. To give the results in my second paper (the paper was not published and the data do not appear in the abstract).

| No. | $KClO_3$ taken. Grms. | Oxygen evolved. Per cent. | KCl formed. Per cent. | Amount of oxygen to 74·5 of KCl. |
|---|---|---|---|---|
| 1 .. .. | 4·3782 | 3·60 | 11·58 | 23·16 |
| 2 .. .. | 6·865 | 1·27 | 4·73 | 20·00 |
| 3 .. .. | 9·291 | 1·61 | 6·00 | 19·99 |
| 4 .. .. | 4·759 | 1·60 | 6·14 | 19·41 |
| 5 .. .. | 4·4905 | 1·47 | 4·84 | 22·63 |
| 6 .. .. | 6·050 | 0·80 | 2·18 | 27·34 |

I heated more gently and carefully than Frankland and Dingwall, and so obtained a higher yield of perchlorate and less free oxygen than they appear to have done. The equation $22KClO_3 = 14KClO_4 + 8KCl + 5O_2$ demands 20 parts of oxygen to 74·5 of KCl.

I was very careful to point out in my former paper that no equation represents the decomposition of potassium chlorate, and only proposed the two I have submitted as marking the usual limits of the final products.

The results with perchlorate given in my second paper were:—

| No. | $KClO_4$ taken. Grms. | Oxygen lost. Per cent. | KCl formed. Per cent. | Amount of oxygen to 74·5 KCl. |
|---|---|---|---|---|
| 1 .. .. | 2·4355 | 3·10 | 2·97 | 77 76 |
| 2 .. .. | 3·8825 | 4·47 | 4·41 | 75·59 |
| 3 .. .. | 1·850 | 7·30 | 7·82 | 69·55 |
| 4 .. .. | 1·217 | 35·21 | 40·33 | 65·04 |

Frankland and Dingwall have failed to notice the first high ratio of oxygen to KCl, by again driving off too much oxygen, and to this extent their results are incomplete.

It is obvious that perchlorate of potassium, when it loses more oxygen than expressed by the equation—

$$KClO_4 = KCl + 2O_2,$$

must be forming a lower oxide of potassium chloride; and the only such oxide possible under the circumstances is the chlorate. Hence the necessity for determining the chlorate formed disappears.

### Discussion.

Dr. Percy Frankland said that he regretted Dr. Teed was not present at the reading of his and Mr. Dingwall's paper, for he would then have clearly understood that they had in no way arrogated to themselves the originality of the experiments, which undoubtedly belonged to Dr. Teed. Their experiments had been made with the view of testing the correctness of Dr. Teed's results, and they had endeavoured to place these results beyond the possibility of doubt, not only by taking special precautions in the method of decomposing the salts, but also by actually determining the proportion of chlorate formed in the decomposition of perchlorate, and the proportion of perchlorate in the decomposition of chlorate.

15. "*The Formation of Ethylic Cyanacetoacetate.*" By Dr. J. William James, University College, Cardiff.

If 50 grms. (1 mol. proportion) of ethylic monochloracetoacetate be mixed with 40 grms. (2 mol. proportions) of potassium cyanide, and 600 c.c. of 99½ per cent alcohol, a reaction takes place slowly at the ordinary temperature, the product consisting of ethylic potassium cyanacetoacetate, $CH_2(CN)\cdot CO\cdot CHK\cdot COOEt$.

If an aqueous solution of this salt be acidified with dilute chlorhydric acid, *ethylic cyanacetoacetate* separates as a colourless oil, which solidifies, if cooled, to a mass of fine silky needles, melting at 26·5° C. It cannot be distilled under ordinary pressure.

*Ethylic dichloracetoacetate* and potassium cyanide interact under the same conditions in a totally different manner, forming *potassium dichloracetate* and ethylic acetate.

16. "*The Relation of Diazobenzene Anilide to Amidoazobenzene.*" By R. J. Friswell and A. G. Green.

In a previous communication to the Society (*Trans.*, 1885, 917) we have attempted to give a partial explanation of the manner in which the isomeric change of diazobenzene anilide into amidoazobenzene takes place. We have shown that, in all probability, previous to the conversion, a resolution of the molecule of the anilide into diazobenzene and aniline is brought about by the acid present, and that these bodies then reunite in a different manner to form amidoazobenzene.

Further than this we could not go, for it still appeared to us a mystery how it was possible that the anilide could be formed under conditions which ultimately led to its resolution and recombination in a new form, for example, when 1 mol. proportion of HCl is present.

This last difficulty has now been cleared away by the suggestions lately put forward by O. Wallach (*Annalen*, ccxxxv., 233), and the whole reaction now appears perfectly clear and straightforward. Diazobenzene combines with aniline *at once* when no excess of mineral acid is present to form diazobenzene anilide; the presence of free mineral acid, however, lessens the tendency to displacement of the amidogen hydrogen, and thus prevents (more or less completely according to the quantity of acid present) the formation of the anilide: under these conditions the tardier tendency to displacement of the para-hydrogen of the nucleus now comes into play and amidoazobenzene is *very slowly* formed. If only 1 mol. proportion of HCl is present, the anilide is formed, but not quantitatively, the acid, though not sufficient to entirely counterbalance the tendency to displacement in the $NH_2$, yet keeps apart a certain quantity of the diazobenzene and aniline, which in course of time interact to form amidoazobenzene and are consequently removed. The conditions are thus altered, and equilibrium is again established by the resolution of a further quantity of the anilide, the constituents of which slowly combine as before to produce amidoazobenzene. In this way the whole of the anilide is slowly resolved and the products recombined to form the compound, which, although the most stable under the conditions, requires a considerable time for its production, thus allowing of the intermediate production of a more quickly formed but less stable body.

17. "*Note on Wallach's Explanation of the Isomeric Transformation of Diazoamidobenzene into Amidoazobenzene.*" By R. Meldola, F.R.S.

In a recent paper published by Wallach (*Annalen*, ccxxxv., 233), that author, who has contributed such valuable results to the chemistry of the azo- and diazo-compounds, puts forward an explanation of the transformation of diazoamido- into amidoazobenzene, which seems to me to call for some comment. I should have been unwilling to call in question any opinion emanating from such a well-known authority had it not been for the somewhat dogmatic statement,—that in the opinion of the writer the question now appeared to have received its final dismissal ("*ihre endgültige Erledigung*"). As such a statement is calculated to induce a feeling of false security on the part of those who have paid attention to

this most interesting case of isomeric change, I take the opportunity of putting upon record my own conviction that the explanation advanced does not materially contribute to the solution of the problem. According to Wallach's view the reason why amidoazobenzene is not formed as the first products is because the aniline upon which the diazo-salt acts is for the most part free, *i.e.*, its $NH_2$-group is not saturated, and the diazobenzene residue can therefore readily enter the group in place of one H-atom. But when the diazoamido-compound is in presence of excess of acid (or of easily decomposable salts) it becomes resolved into its constituents, and these then reunite in a different way, because the $NH_2$-group is saturated and the diazobenzene residue prefers entering the nucleus (in the para-position). The aniline *salt* is in this case, according to the author, in the same condition as a tertiary amine or a phenol. A little consideration will, however, show that the known facts will not bear this interpretation, for diazoamidobenzene is *always* the first product whenever diazobenzene chloride acts upon any mixture of aniline and aniline hydrochloride, and this shows a distinct preference for the amido-hydrogen of the free aniline to be first displaced. In the presence of aniline hydrochloride, on the view that the acid of this salt decomposes the diazoamido-compound into its constituents, we have therefore a mixture of diazobenzene chloride, aniline hydrochloride, and free aniline, *i.e.*, the conditions are precisely the same as at the commencement of the experiment. Why under these reproduced conditions the diazobenzene chloride should now prefer attacking the para-H-atom of the aniline hydrochloride instead of the amido-H of the aniline, remains, after the proposed "explanation," as great a mystery as ever.

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At the next meeting on March 3 there will be a ballot for the election of Fellows, and the following papers will be read:—

"The Colouring-matter of *Drosera Whittakeri*," by Prof. E. H. Rennie, D.Sc.

"Anhydracetone Benzil," by F. R. Japp, F.R.S., and Cosmo Innes Burton, B.Sc.

"Condensation of Benzil with Ketones," by the same.

"Constitution of Glycosine," by F. R. Japp, F.R.S., and E. Cleminshaw, M.A.

"Diphenylglyoxaline and its Homologues, by F. R. Japp, F.R.S.

"Dehydracetic Acid," by Dr. W. H. Perkin, Junr.

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# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 3, January 17, 1887.

**The Laws of the Absorption of Light in Crystals, and a Novel Method for Distinguishing in a Crystal Certain Absorption-Bands belonging to Different Bodies.**—H. Becquerel.—1. The absorption-spectrum observed through a crystal varies with the direction of the rectilinear luminous vibration which propagates itself in this crystal. 2. The bands or rays observed through the same crystal have, in the spectrum, fixed positions, their intensity alone varying. 3. For a given band or ray there exist in the crystal three rectangular directions of symmetry, according to one of which the band generally disappears, so that for a suitable direction of the luminous vibrations the crystal no longer absorbs the radiations corresponding to the region of the spectrum where the band in question appeared. These three directions may be called the principal directions of absorption, relative to this band. 4. In the orthorhombic crystals, by a necessary consequence of crystalline symmetry, the principal directions of absorption of all the bands coincide with the three axes of symmetry. We may thus observe three principal absorption-spectra. In uniaxial crystals the number of absorption-spectra is reduced to two. 5. In clinorhombic crystals one of the principal directions of absorption of each crystal coincides with the only axis of symmetry; the two other principal rectangular directions of each band may be found variously disposed in the plane normal to this axis. Most commonly these principal directions are very near to the principal corresponding directions of optical elasticity. 6. In various crystals the characters of the absorption phenomena differ strikingly from those which we might expect to find after an examination of the optical properties of the crystal. We have just seen that in clinorhombic crystals the principal absorption directions of certain bands were completely different from the axes of optical elasticity of the crystal for the corresponding radiations. If we examine this anomaly we perceive that the crystals manifesting these effects are complex bodies, formed of various matters, one, or sometimes several, of which absorb light and give each different absorption-bands. Now M. de Senarmont has shown that the geometric isomorphism of certain substances does not necessarily involve identity of optical properties, and in particular in the directions of the axes of optical elasticity in relation to the geometric directions of the crystal. In a crystal containing a mixture of isomorphous substances each substance brings its own influence, which may be made to predominate in turn according to the proportions of the mixture. We may, therefore, admit that the molecules of each substance enter into the crystal retaining all the optical properties which they would have if each crystallised separately. The principal directions of optical elasticity are given by the resultant of the actions which each of the component substances exerts on the propagation of light, whilst the aborption of a given region of the spectrum is due to a single one of these substances, and may have for its directions of symmetry the directions which it would have in the absorbing molecule supposing it isolated. It may happen that these directions do not coincide with the axes of optical elasticity of the compound crystal. If such is the cause of the anomaly of certain principal directions of absorption, the bands which present these anomalies must belong to substances different from those which yield bands having other principal directions of absorption. If so, we are in possession of a novel method of spectral analysis which permits us to distinguish in certain crystals bands belonging to different matters, isomorphous, but not having the same optical properties. Two bands appearing in a crystal with common characters but presenting in another crystal characters essentially different must also be ascribed to two different bodies.

**Formation-Heat of certain Sodium Alcoholates.**—M. de Forcrand.—Not capable of useful abstraction.

**On certain Combinations of Stannic Oxide.**—A. Ditte.—The gelatinous stannic acid obtained on decomposing stannic chloride by an alkali dissolves readily in hot sulphuric acid diluted with 8 to 10 vols. of water. The solution deposits crystals having the composition $SnO_22(SO_3HO)$. Gelatinous stannic acid, air-dried, becomes a hard vitreous mass, which if finely powdered dissolves entirely in a hot mixture of equal parts of sulphuric acid and water. The solution deposits crystals of the same composition as the former. The pulverulent metastannic acid obtained by the action of tin upon nitric acid dissolves in hot sulphuric acid diluted with double its volume of water, but more slowly. The compound formed has still the same composition. Anhydrous stannic oxide prepared by igniting any of the hydrates for a few minutes is attacked very slowly by sulphuric acid at a heat near its boiling-point. The resulting salt has still the same composition. If the acid is not in excess,

the liquid, on the addition of an excess of anhydrous ether, deposits a precipitate of the composition $SnO_2(SO_3HO)$. With selenic acid a similar compound is obtained more readily.

**Action of certain Non-Metallic Elements upon Solutions of Silver and Copper Nitrates.**—J. B. Senderens.

**Composition of the Grain of Starch.**—E. Bourquelot.—The grain of starch does not consist of one chemical species, nor of two such (granulose or amylose), but of a larger number of carbo-hydrates.

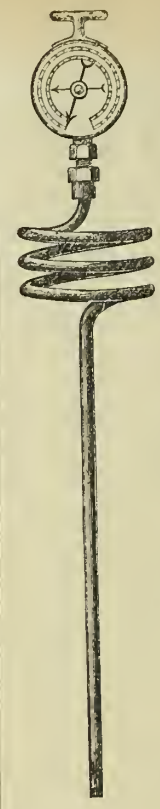
## MISCELLANEOUS.

**Sanitary Institute of Great Britain.**—The Right Hon. G. Sclater Booth, M.P., has accepted the Presidentship of the Congress of this Institute, to be held at Bolton in September next.

**Soap and Alkali.**—We are requested to state that a special course of six lectures on this subject will be commenced by Prof. Meldola, F.R.S., on Wednesday evening, March 23, at 7 o'clock. The syllabus of the course can be had on application at the Finsbury Technical College, Leonard Street, City Road, E.C.

## MEETINGS FOR THE WEEK.

MONDAY, 28th.—London Institution, 5.
—— Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "Building Materials," by W. Y. Dent, F.C.S.
TUESDAY, March 1st.—Institution of Civil Engineers, 8.
—— Royal Institution, 3. "Function of Respiration," by Prof. Arthur Gamgee, F.R.S.
—— Society of Arts, 8. "The Colonial and Indian Exhibition," by Edward Cunliffe Owen, C.M.G.
—— Royal Medical and Chirurgical, 8. (Anniversary).
WEDNESDAY, 2nd.—Society of Arts, 8. "The Cultivation of Tobacco in England," by E. J. Beale.
THURSDAY, 3rd.—Royal, 4 30.
—— Pathological, 8 30.
—— London Institution, 6.
—— Royal Institution, 3. "The Critics of the Age of Anne," by Edmund Gosse, M.A.
—— Chemical, 8. "The Colouring-matter of Drosera Whittakeri," by Prof. Rennie. "Anhydracetonebenzil," by F. R. Japp and C. I. Burton, B.Sc. "Condensation of Benzil with Ketones," by the same. "The Constitution of Glycosine," by F. R. Japp and E. Cleminshaw, M.A. "Diphenylglyoxaline and its Homologues," by F. R. Japp. "Dehydracetic Acid," by Dr. W. H. Perkin, Jun.
FRIDAY, 4th.—Royal Institution, 9. "Brain Surgery in the Stone Ages," by Victor Horsley, F.R.S., F.R.C.S.
—— Society of Arts, 8. "Our Trade Routes to the East," by Major-General Sir F. J. Goldsmid, K.C.S.I., C.B.
—— Geologists' Association 8.
SATURDAY, 5th.—Royal Institution, 3. "Sound," by the Right Hon. Lord Rayleigh.

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THE CHEMICAL NEWS.

Vol. LV. No. 1423.

## GENESIS OF THE ELEMENTS.*

By WILLIAM CROOKES, F.R.S., V.P.C.S.

(Concluded from p. 87.)

But it may be asked, What is the bearing of all this upon the great question of the genesis of the elements? Have we chemists merely discovered some new "elements," or found out that a body hitherto held to be simple is in reality complex? We have, I submit, done something decidedly different. If a metal which is found to have a fixed atomic weight is discovered to be a compound or a mixture, our best test for recognising an element, so-called, has melted away! Hitherto it has been considered that if the atomic weight of a metal, determined by different observers, setting out from different compounds, was always found to be constant (within, of course, the limits of experimental error), then such metal must rightly take rank among the simple or elementary bodies. We learn from Nordenskiold's gadolinium that this is no longer the case. Again, we have here wheels within wheels. Gadolinium is not an element, but a compound, or rather, perhaps, a mixture of yttrium, erbium, and ytterbium. We have shown that yttrium is a complex of five or more new constituents. And who shall venture to gainsay that each of these constituents, if attacked in some different manner, and if the results were submitted to a test more delicate and searching than the radiant-matter test, might not be still further divisible! Where, then, is the actual ultimate element? As we advance it recedes like the tantalising mirage lakes and groves seen by the tired and thirsty traveller in the desert. Are we in our quest for truth to be thus deluded and baulked? The very idea of an element, as something absolutely primary and ultimate, seems to be growing less and less distinct.

But we have by no means done with the rare earths and their lessons. How is it that these bodies are found, as we actually find them, associated in certain rare minerals such as samarskite and gadolinite, but occurring only in a few localities? This fact is hard to account for on the ordinary theories of the origination of the elements.

I venture provisionally to conclude that our so-called elements or simple bodies are, in reality, compound molecules. To form a conception of their genesis I must beg you to carry your thoughts back to the time when the visible universe was "without form and void," and to watch the development of matter in the states known to us from an antecedent something. What existed anterior to our elements, before matter as we now have it, I propose to name *protyle*.†

But how can we suppose the protyle, or fire-mist, converted into the atomic condition? In amorphous matter we recognise a tendency to aggregation not to be identified with gravitation, since it is manifested among finely-divided matter, whether suspended in a medium of a specific gravity superior, equal, or inferior to its own. This agglutinative action is familiar to observers of natural phenomena. Clouds contracting to that appearance known as a mackerel sky; particles of carbon floating in the air, collecting, and ultimately falling as "blacks"; chemical precipitates, at first finely amorphous, but gradually becoming flocky, granular, and crystalline; vortex rings, suddenly quickening out of amorphous smoke;—all these, and many more, exemplify that universal formative principle in nature which I suggest first made itself manifest in the condensation of protyle into atomic matter.

A few weeks ago in this theatre Sir William Thomson asked you to travel back with him an imaginary excursion of about twenty million years. He pictured to you the moment immediately before the birth of our sun, when the Lucretian atoms rushed from all parts of space with velocities due to mutual gravitation, and, clashing together, formed in a few hours an incandescent fluid mass, the nucleus of a solar system with thirty million years of life in it. I will ask you to accompany me to a period even more remote,—to the very beginning of time, before even the chemical atoms had consolidated from the original *protyle*. Let us imagine that at this primal stage all was in an ultra-gaseous state—a state differing from anything we can now conceive in the visible universe.

Now unless the expression "fire-mist" and the supposition that pristine matter was once in an intensely heated condition* are quite misleading and baseless, we have to deal with a process analogous to cooling. This operation, probably internal, reduces the temperature of the cosmic *protyle* to a point at which the first step in granulation takes place; matter as we know it comes into existence, and atoms are formed. As soon as an atom is formed out of *protyle* it is a store of energy, kinetic (from its internal motions) and potential (from its tendency to coalesce with other atoms by gravitation or chemically). To obtain this energy the neighbouring *protyle* must be laid under contribution, *i.e.*, must be refrigerated by it, thereby accelerating the subsequent formation of other atoms. With the birth of gravitating matter, rushing suddenly together from every point of space, we thus get Sir William Thomson's incandescent mass which is presently to cool down into a solar system. We cannot tell if electricity existed prior to the origin of the atomic condition of matter, but with the formation of atomic matter the other forms of energy which require matter in order to manifest themselves, begin to act, amongst others that form of energy which has for one of its factors that which we now speak of as atomic weight.

We have now to seek how protyle was converted not into one only kind of matter but into many. If we recognise that it contained within itself the potentiality of all atomic weights, how did these potentialities become

* A Lecture delivered at the Royal Institution, on Friday Evening, February 18th, 1887.

† We require a word, analogous to protoplasm, to express the idea of the original primal matter existing before the evolution of the chemical elements. The word I have ventured to use for this purpose is compounded of πρό (*earlier than*) and ὕλη (*the stuff of which things are made*). The word is scarcely a new coinage, for in the "Wisdom of Solomon" (xi, v. 17) we read:—"Thy almighty hand, that created the world—ἐξ ἀμόρφου ὕλης—out of formless stuff," the word here rendered "stuff" being in the original ὕλης, from which I have ventured to coin the word "protyle." Six hundred years ago Roger Bacon wrote in his *De Arte Chymiæ*, "The elements are made out of ὕλη, and every element is converted into the nature of another element." Professor Huxley reminds me that ὕλη, in the general sense of material substance, was first used by Aristotle, in whose works it is of very frequent occurrence. In fact the fundamental distinction in his Physical Philosophy is between ὕλη, or *matter*, and εἶδος, or *form*, which last pretty nearly answers to what we should call the sum total of the qualities, powers, and tendencies of a thing—or of forces as the cause of these. In the metaphysics and elsewhere Aristotle distinguishes (1) Πρώτη ὕλη, "Materia Prima," or matter undifferentiated into elements, without form, in fact, and consequently αγνωστος, unknown and unknowable, and (2) ἐσχατη ὕλη, secondary or formed matter, such as earth, or metal, or water, or any other raw material with which we are familiar.

* I am constrained to use words expressive of high temperature but I confess I am unable clearly to associate with *protyle* the idea of hot or cold. *Temperature*, *radiation*, and *free cooling* seem to require the periodic motions that take place in the chemical atoms; and the introduction of centres of periodic motion into protyle would involve its being so far changed into chemical atoms. Probably the first operation was more analogous to the formation of vortex rings than to a reduction of temperature.

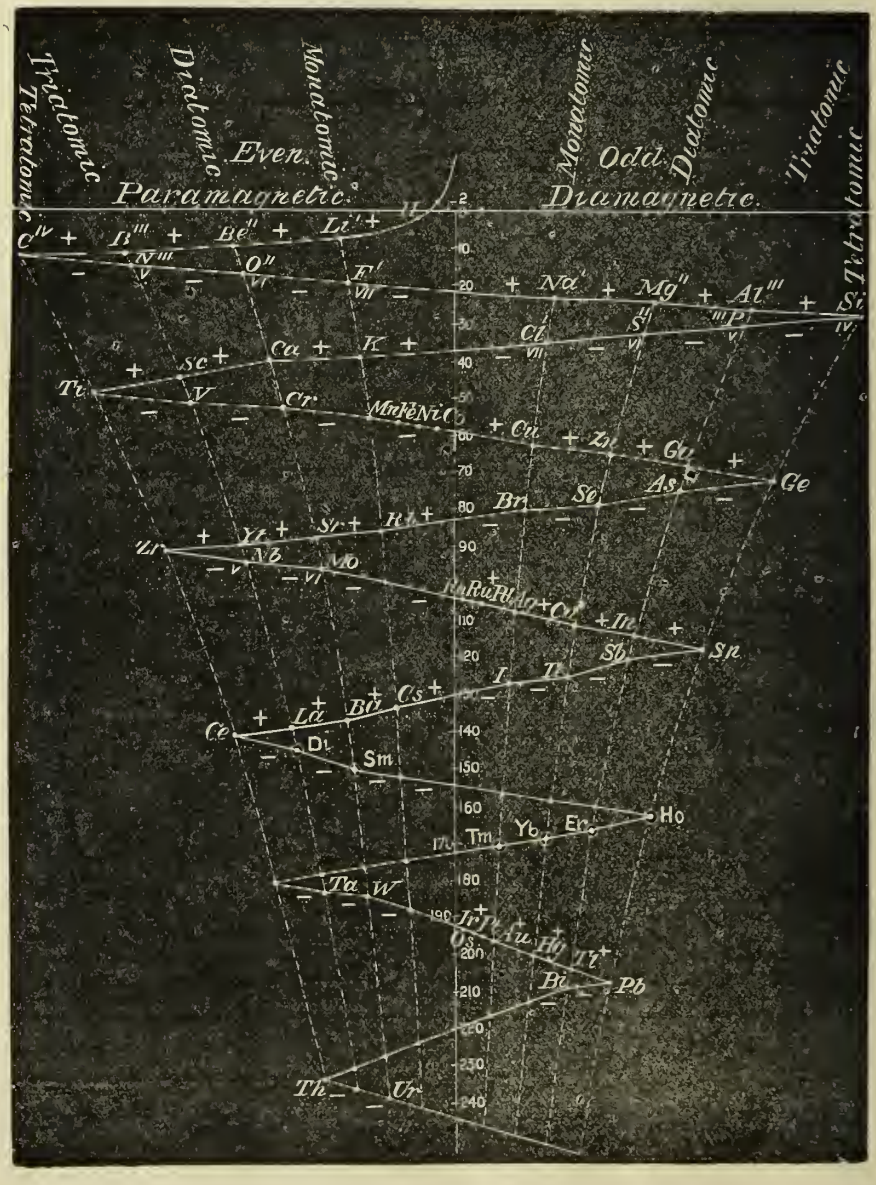
actual? We may here call to mind the suggestion of Dr. E. J. Mills, that our elements are the result of successive polymerisations during the cooling process. We shall also derive much assistance from a method of illustrating the periodic law proposed by my friend Prof. Emerson Reynolds, of the University of Dublin.

I must call your attention to a diagram (Fig. 5) in

The chemical elements are arranged in order, according to their atomic weights, on the centre vertical line which is divided into equal parts.

Following the curve from hydrogen downwards, we see that the elements forming the eighth group of Mendeleeff's arrangement are situate near three of the ten nodal points. This eighth group is divided into the three triplets—iron,

Fig. 5.




which I have slightly modified the original design of Prof. Reynolds. I have represented the pendulum swing as gradually declining in amplitude according to a mathematical law. I have further interposed between cerium and lead another half swing of the pendulum. This renders the oscillations more symmetrical and brings gold, mercury, thallium, lead, and bismuth to the side where they are fully in harmony with members of previous groups.

nickel, and cobalt; rhodium, ruthenium, and palladium; iridium, osmium, and platinum.

These bodies are interperiodic because their atomic weights exclude them from the small periods into which the other elements fall, and because their chemical relations with some members of the neighbouring groups show that they are probably interperiodic in the sense of being in transition stages.

Notice how accurately the series of like bodies fits into

this scheme. Beginning at the top, run the eye down analogous positions in each oscillation, taking either the electro-positive or electro-negative swings :—

Any well-defined element may be likened to a platform of stability, connected by ladders of unstable bodies. In the first coalescence of the primitive stuff there would be

TABLE II.

VERTICAL SERIES OF THE ELEMENTS.

| EVEN. | | | | | | | ODD. | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| iv. | iii. | iii. v. | ii. | ii. vi. | i. | i. vii. | i. vii. | i. | ii. vi. | ii. | iii. v. | iii. | iv. |
| C | B | N | Be | O | Li | F | Cl | Na | S | Mg | P | Al | Si |
| Ti | Sc | V | Ca | Cr | K | Mn | Br | Cu | Se | Zn | As | Ga | Ge |
| Zr | Yt | Nb | Sr | Mo | Rb | — | I | Ag | Te | Cd | Sb | In | Sn |
| Ce | La | — | Ba | Sm | Cs | — | — | — | — | — | — | — | — |
| — | — | — | — | — | — | — | — | Au | — | Hg | Bi | Tl | Pb |

Notice, also, how orderly the metals discovered by spectrum analysis fit in their places—gallium, indium, and thallium ; rubidium and cæsium.

The symmetry of nearly all this series proclaims at once that we are working in the right direction. Much also may be learned from the anomalies here visible. A few bodies, such as didymium, erbium, thulium, and ytterbium, are out of place, and require to have their atomic weights re-determined.

The more I ponder over the arrangement of this zigzag curve, the more I become convinced that he who fully grasps its meaning holds the key to unlock some of the deepest mysteries of creation. As Mr. Browning puts it in his "Parleyings"—"'Tis Man's to explore Up and down, inch by inch, with the taper his reason." Let us batter at the door of the Unknown and do our utmost to get a glimpse of some few of the secrets so darkly hidden.

Let us return in imagination to præ-geological ages, before the sun himself had been aggregated from the original protyle. We require two very reasonable postulates : let there be granted an antecedent form of energy having periodic cycles of ebb and swell, rest and activity. Let there also be granted an internal action akin to cooling operating slowly in the protyle. The first-born element would, in its simplicity, be most nearly allied to protyle. This is hydrogen, of all known bodies the simplest in structure and of the lowest atomic weight. For some time hydrogen would be the only existing form of matter (in our sense of the term). Between hydrogen and the next-formed element there would be a gap in time, and in the interval the element standing next in order of simplicity would gradually be approaching its birth-point. In this interval we may suppose that the evolutionary process soon to determine the birth of a new element would fix likewise its atomic weight, its affinities, and its chemical position.

In this genesis of the elements the longer the time taken up in the cooling-down process during which the hardening of protyle into atoms takes place, the more sharply defined would be the resulting elements ; whilst the more rapid and the more irregular the cooling the more closely the resulting bodies would fade into each other by almost imperceptible degrees. Thus we may conceive that the succession of events which gave rise to such groups as platinum, osmium, and iridium,—palladium, ruthenium, and rhodium,—iron, nickel, and cobalt, —might have produced only one element in each of these three groups if the process had been greatly prolonged. And conversely, had the rate of cooling been much more rapid, elements might have originated still more nearly identical than are nickel and cobalt. Thus may have arisen the closely allied elements of the cerium, yttrium, and similar groups. In fact, we may regard the collocation of the minerals of the class of samarskite and gadolinite as a kind of cosmical lumber-room where elements in a state of arrested development—the unconnected missing links of inorganic Darwinism—are gathered together.

formed the smallest atoms ; these would then unite, forming larger groups ; the gaps between the several stages would gradually be bridged over, and the stable element appropriate to that stage would absorb, so to speak, the unstable rungs of the ladder which led up to it. It may be questioned whether there is an absolute uniformity in the mass of every ultimate atom even of one and the same chemical element. Probably our atomic weights merely represent a mean value around which the actual atomic weights of the atoms vary within certain narrow limits. When, therefore, we say that, *e. g.*, the atomic weight of calcium is 40, the actual fact may well be that whilst the majority of the calcium atoms really have the atomic weight of 40, some are represented by 39·9 or 40·1, a smaller number by 39·8 or 40·2, and so on. The properties which we perceive in any element are thus the mean of a number of atoms differing among themselves very slightly, but still not identical.* Is this the true meaning of Newton's "old worn particles" ?

That this speculation, hazardous as it may seem, is in some respects supported by the experimental results above described will, I think, be admitted. It seems to me that the hypothesis I have just suggested, if taken in conjunction with the diagram, Fig. 5, enables us to proceed a step or two further along the track of the evolution of the elements. We may trace in the undulating curve the action of two forms of energy, the one acting vertically and the other vibrating to and fro like a pendulum. Let the vertical line represent temperature gradually sinking through an unknown number of degrees from the dissociation-point of the first-formed element downwards to the dissociation-point of the last member of the scale.

But what form of energy is figured by the oscillating line ? We see it swinging to and fro to points equidistant from a neutral centre. We see this divergence from neutrality confer atomicity of one, two, three, or four degrees as the distance from the centre increases to one, two, three, or four divisions. We see the approach to or the retrocession from this same neutral line deciding the electro-negative or electro-positive character of each element ; those on the retreating half of the swing being positive, and those on the approaching half negative. In short, we are led to suspect that this oscillating power must be closely connected with the imponderable matter, essence, or source of energy we call electricity.

Let us now return to the period just preceding the birth of the first element. Before that time matter as it now is manifested did not exist. We can no more conceive of matter without energy than of energy without matter ; indeed, from one point of view the two are convertible terms. Let us assume that simultaneously with the creation of atoms all those attributes which enable us to

* I venture to suggest that the heavier and lighter atoms formed from the protyle may have been partially sorted out by a process in nature somewhat analogous to the fractionation which has been already described. Such a sorting out would be effected chiefly whilst atomic matter was condensing from the primal state ; but it may also have been carried on during geological ages in the wet way by successive solutions and re-precipitations of the various earths.

discriminate one form of matter from another, start into being endowed with energy.

Our pendulum begins its swing from the electro-positive side: lithium, next to hydrogen in the simplicity of its atomic weight, is now formed, followed by glucinum, boron, and carbon. Each element, at the moment of birth, takes up definite quantities of electricity, and on these quantities its atomicity depends.* Thus are fixed the types of the monatomic, diatomic, triatomic, and tetratomic elements.

It has been pointed out by Dr. Carnelley that "those elements belonging to the even series of the periodic classification are always paramagnetic, whereas the elements belonging to the odd series are always diamagnetic." Now in our curve the even series to the left, so far as has been ascertained, are paramagnetic, whilst, with a few exceptions, all to the right are diamagnetic. The strongly magnetic group, iron, manganese, nickel, and cobalt, lie close together on the proper side. But the interperiodic groups, of which palladium and platinum are respectively examples, are supposed to be feebly magnetic. If this can be verified they form exceptions which have yet to be explained. Oxygen, which weight for weight is even more strongly magnetic than iron, lies near the beginning of the curve, whilst at the opposite end come the powerfully diamagnetic metals, bismuth and thallium.

We come now to the return or negative part of the swing: nitrogen appears and shows instructively how position governs the mean dominant atomicity. Nitrogen occupies a position immediately below boron, a triatomic element, and, therefore, nitrogen is likewise triatomic. But nitrogen also follows upon carbon, a tetratomic body, and occupies the fifth position if we count from the place of origin. Now these seemingly opposing tendencies are beautifully harmonised by the endowment of nitrogen with a double atomicity, its atom being capable of acting either as a tri- or as a pentatomic element. With oxygen (di- and hexatomic) and fluorine (mon- and heptatomic) the same law holds good, and one half oscillation of the pendulum is completed. Passing the neutral line again, we find successively formed the electro-positive bodies sodium (monatomic), magnesium (diatomic), aluminium (triatomic), and silicon (tetratomic).

Here we may notice a curious coincidence; at the beginning of this part of the curve stands carbon, the most ubiquitous element in the organic world. At the end, in opposition, stands silicon, the most commonly occurring element in the inorganic sphere. Further, as we move towards the median line, carbon is successively followed by nitrogen, oxygen, and fluorine, all entering into organic compounds and all gaseous in the free state. If we work back from silicon we find aluminium, magnesium, and sodium all much less disposed to volatility, and all very prominent members of the mineral kingdom.

The first complete swing of the pendulum is accomplished by the birth of the three electro-negative elements, phosphorus, sulphur, and chlorine; all three, like the corresponding elements on the opposite homeward swing, having at least a double atomicity, depending on position.

Let us pause and examine the results. We have now formed the elements of water, of air, of ammonia, of carbonic acid, of plant and animal life; we have phosphorus for the brain, salt for the sea, clay and sand for the solid earth; two alkalies, an alkaline earth, an earth, along with their carbonates, borates, nitrates, fluorides, chlorides, sulphates, phosphates, and silicates, sufficient, it may be said, for animal and vegetal life, and for a world not so very different from that in which we live and move.

Again let us follow our pendulum. After the formation of chlorine this pendulum touches the neutral line, and is in the same position as in the beginning. Had everything remained as at first the next element to appear would again have been lithium, and the original cycle would have been eternally repeated, producing again and again the same fifteen elements. The conditions, however, are no longer the same: time has elapsed and the form of energy represented by the vertical line has declined; in other words, the temperature has sunk, and the first element to come into existence when the pendulum starts for its second oscillation is not lithium, but the metal next allied to it in the series, *i.e.* potassium, which may be regarded as the lineal descendant of lithium, with the same hereditary tendencies, but with less molecular mobility and a higher atomic weight.

Pass along the curve and in nearly every case the same law holds good. Thus the last element of the first complete vibration is chlorine. In the corresponding place in the second vibration we have not an exact repetition of chlorine but the very similar body bromine, and when the same position recurs for a third time we see iodine. I need not multiply examples. I may, however, point out that we have here a phenomenon which reminds us of alternating or cyclical generation in the organic world, or we may perhaps say of atavism, a recurrence to ancestral types, somewhat modified.

In this evolutionary scheme it cannot be expected that the potential elements should all be equal to each other. On the contrary, many degrees of stability will be represented, and if we look with a scrutinising eye we shall see our old friend the "missing link," coarse enough to be detected in the groups comprising such bodies as iron, nickel, and cobalt; palladium, ruthenium, and rhodium; iridium, osmium, and platinum; whilst in a more subtile form these missing links present themselves as representatives of the differences which I have suggested between the atoms of the same chemical element.

On the even or para-magnetic half of the swing the energy appears to have acted in a very irregular manner, whilst on the odd, or dia-magnetic half, there is considerable regularity. Thus, between the extreme odd elements, silicon (28), germanium (73), tin (118), a missing element (163), and lead (208) there is a difference of exactly 45 units, rendering this half of the curve remarkably symmetrical. On the even side the differences are 36, 42, 51, 39, and 53 (assuming an atomic weight of 180 for a missing element between cerium and thorium). At first sight these differences appear to follow no law, but they gain interest when we see that the mean difference of these figures is 44·2—almost exactly the same as that on the odd side of the curve.

From this uniformity of difference—actual on the one side and average on the other—we may fairly infer that whilst on the odd side there has been little or no variation in the force symbolised by the vertical line, minor irregularities have been the rule on the even side. Or, in other words, the fall of temperature has been very uniform on the odd side—where, accordingly, we see that every original element represents a well marked group, sodium, magnesium, aluminium, silicon, phosphorus, and chlorine; whilst on the even side the temperature has fallen with considerable fluctuations, thus preventing the formation here of any well-marked groups of elements, excepting those of which lithium and glucinum are the leading types.

Having thus detected irregularities in the fall of temperature in the protyle, we may next ask is there any fluctuation in the force represented by the pendulum-movement? This movement I have assumed to be connected with electrical energy. The earliest-formed ele-

* "Nature presents us with a single definite quantity of electricity. . . . For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte, which is the same in all cases."—G. Johnstone Stoney, "On the Physical Units of Nature."—*British Association Meeting*, 1874, Section A. *Phil. Mag.*, May, 1881.

"The same definite quantity of either positive or negative electricity moves always with each equivalent ion, or with every unit of affinity of a multivalent ion."—Helmholtz, Faraday Lecture, 1881.

"Every monad atom has associated with it a certain definite quantity of electricity; every dyad has twice this quantity associated with it; every triad three times as much, and so on."—O. Lodge, "On Electrolysis," *British Association Report*, 1885.

ments are those in which chemical energy is at a maximum; as we descend the scale the affinities become feebler and the chemism grows more and more sluggish. In part this change may be due to the circumstance that the elements generated at a reduced temperature no longer possess great molecular mobility. But it is also extremely probable that the chemism-forming energy is itself dying out like the fires of the cosmic furnace. I have attempted to symbolise this gradual fading by a decrease in the amplitude of vibration.

The figures representing the scale of atomic weights may be supposed to represent, inversely, the scale of a gigantic pyrometer plunged into a cauldron where the elements of suns and worlds are undergoing formation. As the heat sinks, the elements generated increase in density and atomic weight. Below the formation-point of uranium the temperature will probably permit of the earlier-born elements of forming combinations among themselves, and we shall witness, *e.g.*, the birth of water, and the formation of those known compounds the dissociation of which is not beyond the powers of our terrestrial sources of heat.

Turning to the upper portion of the diagram we see that there is little room for elements of a lower atomic weight than hydrogen. But let us pass "through the looking-glass" and cross the zero line. What shall we find on the other side? Dr. Carnelley asks for an element of negative atomic weight; and here is ample room and verge enough for a shadow series of such unsubstantialities, leading, perhaps, to that "Unseen Universe" which two eminent physicists have discussed. Helmholtz says that electricity is probably as atomic as matter;* is electricity one of the negative elements? and the luminiferous ether another? Matter, as we now know it, does not here exist; and the forms of energy which are apparent in the motions of matter are as yet only latent possibilities.

A genesis of the elements such as is here sketched would not be confined to our little solar system, but would probably follow the same general sequence of events in every centre of energy now visible as a star.

It may be said that so far I have proved nothing. But I may submit that at least I have shown the improbability of the persistence of the ultimate character, and the eternal self-existence, the fortuitous origin, and the simultaneous creation of the elements. The analogy of these elements with the organic radicles, and still more with living organisms, constrains us to suspect that they are compound bodies, springing from a process of evolution. We have drawn corroborative evidence from the distribution and the association of the rare earths, evidence which seems to be converging to the point of assuming a direct character. Led by the great law of continuity I have ventured to suggest a process by which our elements may have been originated. I do not say *must* have been originated, for no one can be better aware than I am how much remains to be done before this great, this fundamental question can be finally solved. I earnestly hope that others will take up the task, and that chemistry, like biology, may find its Darwin.

If we consider the position we occupy with reference to the primary questions of chemistry, we might compare research to a game of chess. Man, the investigor, is playing, not with Satan for his soul, but with Nature for knowledge and power. Each element has its allotted moves on the great board of the universe; some of them dependent solely on themselves, and others on the interaction of the adjacent elements. Some of our elements may be compared to pawns, others to knights, bishops, or castles. The game is fearfully unequal. Our antagonist knows the power and the limitations of every piece, all the laws of the game, all possible moves, and is merciless in exacting penalty for errors. We experimentalists know nothing but what we have learned in countless losing games. But our knowledge is increasing. Nature no longer gives us fool's mate. The struggle becomes more obstinate, more exciting, we come upon new gambits, new combinations, and though still checkmated at the last, we take a few pawns, perhaps even a piece or two. Such partial successes were achieved when Lavoisier introduced the use of the balance and developed the theory of combustion; when Dalton put forward the atomic theory; when Davy decomposed the alkalies; when Wöhler effected the synthesis of urea; and when Faraday first liquefied a gas. On such and many similar occasions I can imagine our antagonist becoming thoughtful.

But suppose we one day win the game; that we find out what these obstinate elements really are, that we learn how they came into being, and wherefore their number, their properties, and their mutual relations are such as we find them? We shall then know, *d priori*, what we have now to find out by special experiment; we shall foresee the results of every conceivable reaction, and our theories will legitimate themselves by the power of prediction. To attain such knowledge seems to me the grand task of the chemistry of the coming age.

If you think I have given too free rein to the "scientific imagination" you will, I hope, forgive me as one who at least does not despair of the future of our science.

* If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity."—Helmholtz, Faraday Lecture, 1881.

## ON THE PHOSPHORESCENCE OF ALUMINA.

By M. EDMOND BECQUEREL.

M. de Boisbaudran has forwarded to the author two samples of alumina which he had prepared from alminium chloride, and one of which had been ignited by him at a high temperature. This specimen, which in his hands—when excited by electric discharges in a very high vacuum—emitted merely a green light, without a trace of red, gave in the hands of M. Becquerel, in a phosphoroscope under the action of the light of the voltaic arc, an emission of *red* phosphorescent light. This result agrees with all those previously obtained by M. Becquerel with specimens of alumina as pure as possible. As the author intimated, in a recent memoir, the methods of excitation not being the same, it is not surprising that the luminous emission, though from one and the same matter, should be different. In a phosphoroscope we excite the substances directly by means of the rays which are projected upon their surface, and which are comprised between the extreme refrangibilities furnished by the exciting source. In these conditions M. Becquerel has shown that there are two active parts in the solar spectrum giving to alumina, or to the ruby, or to chromated alumina the power of *red* phosphorescence. One portion begins abruptly about D and extends almost to F; the other, less active than the former, extends up to H.

In tubes containing air highly rarefied the electric discharges are scarcely visible, and rays are found comprised between the refrangibilities A and H. It is therefore very probable that the exciting rays are for the greatest part of an extreme refrangibility,—that is to say, of a very small wave-length, rays which are absorbed by a very slight gaseous stratum. These rays excite the alumina differently from the less refrangible rays, and give, possibly, a phosphorescence of green rays of an extremely short duration, less than is necessary for producing an impression in the phosphoroscope. This hypothesis M. Becquerel hopes to verify experimentally.

But without any attempt to show the difference of the effects produced upon alumina by the two above-mentioned methods of experimentation, the author cites the fact that if, in a tube containing rubies, the vacuum is imperfect, they give scarcely a trace of light under the influence of the electric discharges, whilst if the vacuum is rendered

more perfect they become illuminated with a brilliant red light, as they always do in the phosphoroscope.

M. Becquerel has, moreover, demonstrated long ago that though the presence of chrome much intensifies the power of alumina to emit red phosphorescent rays in the phosphoroscope, yet alumina as pure as possible, if similarly treated, gives an emission of rays of the same colour, though of less intensity. It may even be possible that chrome imparts to alumina a different absorptive power for the exciting rays of light, and thus augments its phosphorescent power. There may then be produced an action of the same kind as that possessed by colouring-matters in virtue of which they modify the absorbent power of bodies chemically susceptible to light, and render them sensitive to the action of rays which do not act upon them without this admixture.

The complication of effects observed when employing the discharges in tubes of very rarefied gases, as well as the differences in the duration of the rays emitted by phosphorescence, seem likely to explain the differences presented by one and the same specimen of alumina excited in these tubes, or submitted to the action of the sun or of the voltaic light in a phosphoroscope.—*Comptes Rendus* (civ., p. 334).

## LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1887.

By WILLIAM CROOKES, F.R.S.,

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

and C. MEYMOTT TIDY, M.B., F.C.S.,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

*To* COLONEL SIR FRANCIS BOLTON, *Water Examiner, Metropolis Water Act*, 1871.

London, February 7th, 1887.

SIR,—We submit herewith the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from January 1st to January 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

At the beginning of this year, as at the end of last year, the river was in a swollen and turbid state from the influx of snow-water, carrying with it much clayey matter; and as a result, during the first fortnight of January, as during the last fortnight of December, several samples of the water furnished by three of the Companies drawing their supply from the Thames were, as set forth on Table II., found to be slightly turbid. The latest samples recorded as "very slightly turbid" were taken on the 14th and 15th of the month, one out of the seven taken on each day, since when the water delivered by all the Companies alike has been uniformly bright and well filtered. Throughout the month, the water, except that supplied by the New River Company, was found, when examined in bulk, to present a slightly brownish tint of colour. The proportion of organic matter present, though not high for the season of the year, was appreciably above that of the previous month's supply, the mean amount of organic carbon in the Thames-derived water-supply being 0·199 part in 100,000 parts of the water, corresponding to between three and four-tenths of a grain of organic matter per gallon.

We are, Sir,
Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

## ZINC EISEN.

By H. N. WARREN, Research Analyst.

THE use of this compound, although greatly limited, an in itself being useless as an alloy, on account of its great brittleness, however promises to be of considerable value in pyrotechny, on account of the brilliant and at the same time peculiar light attending its combustion when admixed with other pyrotechnic ingredients; it is also possessed of theoretical interest, since it involves a ready and at the same time simple method of producing an alloy existing between a somewhat highly volatile metal zinc and a non-volatile metal iron; it also furnishes by far the best method of producing finely-divided zinc, in cases where the presence of iron is not objectionable. The best method of preparing the alloy is as follows:—From 1 to 2 lbs. of zinc are raised to the melting-point in a clay crucible, and from 3 to 3½ ozs. of anhydrous sodio-ferrous chloride are thrown on the surface of the molten zinc, the top of the crucible being immediately covered in order to exclude air. A violent reaction immediately takes place, and terminating in the above alloy, in admixture with zinc chloride according to the following equation:—$Zn + FeCl_2 = ZnCl_2 + Fe$. The excess of zinc alloying itself with the reduced iron, forming a highly brittle substance possessing a full metallic lustre, and admiting of being pulverised with the utmost ease. The alloy when performed in this manner seldom varies from 11 to 13 per cent.

## THE QUANTITATIVE DETERMINATION OF BORIC ACID.

By TH. ROSENBLADT.

FOR the determination of free boric acid in substances soluble in water or in acids, or if combined with an alkali or with magnesia, the methods indicated by A. Stromeyer and C. Marignac are found sufficient. The case is different when boric acid must be determined in the course of a complicated analysis, as, for instance, in the silicates. The known methods are then either quite inapplicable or give untrustworthy results.

In the *Zeitschrift* (xiv., p. 360) Ditte proposed a method in which calcium borate is separated out in a form insoluble in water. The author has made use of this process in the analysis of tourmalines, but no concordant results could be obtained.

Upon the whole, direct determinations of boric acid belong to the most complicated operations of analytical chemistry, whence it is usually determined by the inaccurate method of difference.

The characteristic green colouration of a spirit-flame is still commonly employed for the detection of boric acid. This colouration of the flame depends on the dissociation of boric ethyl ether, which boils at 120°. On one occasion the author found this method unsuccessful, on account of the simultaneous presence of copper chloride. He substituted methylic alcohol, and obtained the corresponding boric methyl ether, distinguished by its extra-

ordinary volatility, as it boils at 65°. The reaction came up very distinctly.

The experiment was then modified as follows: the substance was put in a short, wide test-tube, with a little concentrated sulphuric acid; when it was cold methylic alcohol was gradually added, and the tube was closed with a caoutchouc stopper having two perforations. The two apertures receive two glass tubes, one bent at right angles and reaching almost to the bottom of the tube, and the other, ending below the stopper, about 5 c.m. in length and drawn out at the exterior end to 1 m.m. Hydrogen gas (or coal-gas) was passed through the apparatus, and a light was applied to the gas as it escaped. A fine green flame was at once obtained, which, on examination with the spectroscope, shows the characteristic spectrum of boric acid.

This method renders it possible to detect boric acid even in presence of other substances which give a green colour to flame, as with this arrangement a green colouration is produced by boric acid only.

For the quantitative determination of boric acid the author constructed the following apparatus: he took a wide-mouthed Erlenmeyer flask, perfectly dry and holding 100 c.c., closed it with a cork having two perforations; through one of these passed a tube funnel, fitted with a cock and reaching down almost to the bottom of the flask; through the other passed one limb of a condensing-tube: the second limb of the condensing-tube opened into another dry Erlenmeyer flask, which was closed in like manner with a doubly-perforated cork. Through the second perforation of this cork passed one limb of a tube bent twice at right angles, whose second limb was dilated in a globular form and led into a small flask. This last flask contained a little water and ammonium carbonate. The entire apparatus was closed air tight.

The substance under examination, finely powdered and weighed out, is put into the first flask and moistened with methylic alcohol; the flask is then closed with the cork; the funnel tube (with the cock shut) is then filled with sulphuric acid (sp. gr. 1·84), taking twice as much acid as the weight of the substance. After proper arrangements have been made for good refrigeration the sulphuric acid is gradually let drop into the flask by partially opening the cock, and afterwards 10 c.c. of methylic alcohol are gradually introduced in the same manner. The flask is then set in a capacious beaker filled with water, which is heated as long as methylic alcohol distils over; 5 c.c. more methylic alcohol are then added in the same manner through the funnel tube, and the distillation is renewed.

This process is several times repeated, and in general 40 to 50 c.c. of methylic alcohol suffice to volatilise 0·3 grm. boric acid. After the distillation is complete the receiver is taken away, the contents of the small flask added to the distillate; the globe tube is rinsed out, and to the entire liquid are added 10 c.c. of a solution of ammonium carbonate (1 : 10). During the distillation magnesia—about three times as much as the probable amount of boric acid to be determined—is put into a platinum capsule holding 40 to 60 c.c., the capsule is covered with a lid and strongly ignited, and when cold the tare is determined along with the magnesia. As magnesia is very hygroscopic the weighing must be performed very carefully and expeditiously.

The weighed magnesia is then moistened in the capsule with ammonium carbonate, the distillate is introduced into the capsule and carefully evaporated down upon a sheet of asbestos, carefully avoiding loss; the residue is ignited and again weighed.

The increase of weight in the capsule and its contents gives the weight of the boric acid present in the sample.

Compounds insoluble in acids, such as silicates, are opened up with potassium-sodium carbonate before distillation; the melt is then carefully pulverised so as to avoid all loss, and is then distilled, as above directed, with sulphuric acid and methylic alcohol. To remove any particles adhering to the crucible, the author rinses it out with the sulphuric acid about to be used.

Substances containing fluorine, such as tourmalines, are strongly ignited before being opened up; the loss is noted and taken into account in the analysis.

It is scarcely necessary to remark that the sample before being opened up should be in the finest state of division.

In the analysis of minerals, &c., containing chlorine, silver sulphate must be introduced into the Erlenmeyer flask to prevent the evolution of hydrochloric acid.

In these operations only such methylic alcohol must be used as, if heated with sulphuric acid in the water-bath, neither blackens nor evolves sulphurous acid.—*Zeitschrift f. Anal. Chemie* (vol. xxvi., part 1, p. 18).

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## INVESTIGATION OF THE ATOMIC WEIGHT OF TUNGSTEN.

By JOHN WADDELL, Ph.D. (Heidelberg), D.Sc. (Edin.).

Owing to theoretical considerations which need not be here detailed, I was led to doubt the accuracy of the atomic weight of tungsten which has usually been accepted as correct, and an investigation of the literature of the subject did not satisfy me that sufficient care had been taken to ensure the purity of the materials employed. Molybdenum and silica especially are impurities likely to occur, and little evidence was afforded that they were absent in the compounds from which the atomic weight of tungsten was estimated.

The method of purifying by re-crystallisation, though the one almost universally adopted, seemed open to objection, and I decided to try the method of fractional precipitation. In order to carry out this process it was necessary to prepare an alkaline tungstate, and it was advisable to have it as pure as possible before proceeding with the precipitation. It was designed to get a series of precipitates of such a character that, if pure from admixture, tungstic acid could be readily obtained, by the reduction of which to metallic tungsten the data necessary for atomic-weight determination are afforded. Similarity of composition in the precipitates was to be taken as a guarantee of purity; for it was unlikely that impurities present would be thrown down in the same proportion in all the fractionations. If a difference occurred in the precipitates, those at the extremes should be most unlike, while those near the middle should have practically the same composition, and might fairly be accepted as pure. This paper is to be devoted chiefly to a description of how the above plan was carried out, with an account of some of the difficulties encountered and the precautions adopted, together with the results arrived at by the investigation.

Some preliminary experiments were made with scheelite, in order to test methods of separation of silicon and molybdenum, both of which were present in the mineral. Scheelite is essentially calcium tungstate; the sample I worked with also contained iron in some form. The mineral was disintegrated by boiling with aqua regia, and the soluble chlorides filtered off from the portion insoluble in acid. This precipitate was bright yellow in colour, and along with tungstic acid contained considerable silica and a little molybdic acid. Attention was first directed to methods of separating silica, two methods being tried. The first was fusion of the mixture of silica and tungstic acid with potassium hydrogen sulphate, by which operation soluble tungstate (with molybdate when molybdic acid is present) is produced, the silica being unattacked. Details of the operation are given in the Appendix. The solution of tungstate and sulphate having been obtained free from silica, the next step was to precipitate the tungsten in some form.

Theoretically it is possible to precipitate tungstic acid

from a mixture of alkaline tungstate and sulphate by heating with sulphuric acid. In this process care must be taken to regulate the temperature properly, for if too low the tungstic acid does not separate out, and if too high the mass fuses and reproduces the original tungstate. This method, which may be used with small quantities, though even in such cases probably not very satisfactory, did not seem capable of application on the large scale. A method of separation common enough in quantitative analysis is to use mercurous nitrate as a precipitant. Mercurous tungstate is thrown down, and from that precipitate tungstic acid can be obtained either by sublimation of the mercury or by extraction of the latter with aqua regia. I thought that this method might prove of use for fractional precipitation, and proceeded to test it. I found that the mercurous tungstate is difficult to filter, the precipitate having a tendency to run through the paper. The same difficulty presents itself in filtering the tungstic acid obtained by treatment of the mercurous tungstate with aqua regia. These obstacles were not insurmountable, however, for if water containing mercurous nitrate be used for washing the tungstate the filtration can be carried on successfully. In the same way very dilute hydrochloric acid, if used to wash the precipitate of tungstic acid, makes the operation of filtering quite easy.

A much more serious difficulty was presented by the sparing solubility of mercurous salts. It was only possible to make a dilute solution of mercurous nitrate, and even this dilute solution seemed to precipitate sulphate as well as tungstate. I found that mercurous nitrate continued to give a precipitate, though excess of mercury seemed to be present, a test portion of the liquid giving with hydrochloric acid a precipitate of mercurous chloride, as also a precipitate with sulphuretted hydrogen. The use of large quantities of liquid being disadvantageous, this method of separation was abandoned. The second method of separation of silica and tungstic acid tried was digestion with ammonia. The best method for carrying out the operation is described in the Appendix. As a result of my work some ammonium tungstate was obtained, but the extraction of the tungstic acid was not complete. Later experience indicated slight improvements in detail, such as would make the extraction more perfect, but in the meantime a material had been obtained almost free from silica.

Of the preliminary work it only remains to describe the process employed for eliminating the molybdenum. Some of the ammonium tungstate above described, which contained part at least of the molybdenum originally in the scheelite, was changed into the sodium salt by fusion with sodium carbonate. To a solution of tungstate thus obtained enough tartaric acid was added to prevent precipitation of tungstic acid by acidification with hydrochloric acid. A stream of sulphuretted hydrogen, passed for several hours formed a slight precipitate, which gave the borax and microcosmic beads characteristic of molybdenum. The filtrate was evaporated to dryness in a platinum basin, and the mass heated till it began to char. Potassium nitrate was added in small portions till the carbon was all oxidised and a white mass obtained, mainly tungstate, but containing chloride and carbonate as well. These impurities presented no special disadvantages, but the process of evaporation of the tartrate and subsequent ignition with nitre was troublesome.

The process of elimination of silicon and molybdenum seemed, therefore, likely to prove an easy task. I hoped to avoid the difficulty by using as starting-point a material containing neither of these impurities. With this view I procured commercial tungsten, a dark grey powder containing 94 to 98 per cent of the metal. I was assured by the manufacturer that molybdenum was absent. At the outset I was met by the difficulty of getting the material into a workable form. So slowly is it attacked by acids that my attempts to oxidise it by aqua regia were very imperfectly successful. Better results were obtained by throwing a mixture of the metal with nitre into a red-hot crucible. The crucible itself was attacked, however, and a third method was tested. On the small scale the results were good, and considerable attention was devoted to the determination of the most favourable conditions. The method consisted in igniting a mixture of potassium chlorate, sugar, and metal. Evidently what was desired was a high temperature and a large quantity of available oxygen. The proportions found most suitable were—chlorate 9 parts, sugar 3 parts, tungsten 5 parts. The oxidation was in this way very rapid, but from the potassium tungstate thus produced it was almost impossible to get a fair yield of tungstic acid, owing to the presence of the large quantity of other salts. A much more satisfactory mode of oxidation was by the direct action of air at a high temperature. The commercial tungsten was placed in a porcelain tube in a Fletcher's furnace, and heated to redness in a current of air. Fumes of sulphurous acid were evolved, and were absorbed by a caustic soda solution. In this solution molybdic acid was afterwards found, though only in very small quantity. At the end of six hours the tungsten was oxidised to a greenish mass. The colour was due to imperfect oxidation. When the roasting was continued for about thirty hours a yellow powder was obtained, there being very little, if any, unoxidised tungsten. The green substance, however, was quite suitable for further manipulation, as it contained only about 5 per cent of unoxidised material, and this was readily separated.

A preliminary experiment showed that it would be impossible to extract the tungstic acid from the green powder by boiling with solution of caustic soda. I therefore fused it with half its weight of carbonate of soda, digested the fused mass with water, and filtered off from the unoxidised residue. The filtrate was evaporated in a large silver basin with addition of ammonium carbonate, the precipitate formed filtered off, and the filtrate evaporated down as before, the process being repeated till the carbonate produced no more precipitate. The total precipitate was very small, and proved to be chiefly, if not entirely, alumina. During the evaporation a thin copper-coloured film appeared on the silver basin. This film was soluble in hydrochloric acid, giving a blue solution which became decolourised on exposure to the air or addition of a drop of nitric acid. The film was evidently some compound of tungsten, and I believe that titanium salts give similar deposits in platinum vessels.

The clear solution of tungstate, which naturally contained carbonate, was evaporated to small bulk, and thus crystals were obtained. As, however, the mother-liquor was quite colourless and clear, I continued the evaporation to dryness. In this way I prepared nearly 3 kilos. of mixed tungstate and carbonate. In a trial portion of this substance I proved the presence of an appreciable, though small, quantity of molybdenum.

After considerable investigation I was not able to find a more convenient method for separating molybdenum and tungsten than the one already given, which is recommended by Rose. I found, however, that the subsequent elimination of tartaric acid was unnecessary for my purpose. I discovered that, while the presence of no very large quantity of this acid prevents the precipitation of tungstic acid by *cautious* addition of a *little* hydrochloric acid, a considerable excess of the latter, even if slowly added, gives a precipitate. This precipitate can be re-dissolved by tartaric acid in *large* excess *only*, but, once re-dissolved, *much* hydrochloric acid can be added before precipitation again occurs.

A solution of 300 grms. of tunstate was added to a solution of 150 grms. of tartaric acid, and the molybdenum separated as above described. The filtrate had a blue colour, evidently due to some reduction of the tungstate; but a current of air passed for several hours through the solution decolourised the liquid, which was then ready for fractional precipitation.

(To be continued.)

# PROCEEDINGS OF SOCIETIES.

## PHYSICAL SOCIETY.

*Special General Meeting, February 26, 1887.*

Prof. W. G. Adams, Vice-President, in the Chair.

The Resolution passed at the meeting on February 12th, providing greater facilities to persons living abroad for qualifying for membership of the Society was unanimously confirmed. The meeting was then resolved into an ordinary one, at which Prof. W. Stroud and Mr. G. S. Gulbenkian were elected Members of the Society.

Mr. James Swinburne read a "*Note on Prof. Carey Foster's Method of Measuring the Mutual Induction of Two Coils.*"

The author described an apparatus devised last summer for measuring mutual induction by a null method, thus dispensing with a ballistic galvanometer. The induction in the secondary coil is balanced by an opposite effect produced by a variable known fraction of the primary current passing through one wire of a double-wound coil of known mutual induction, the other wire of which is joined in series with the secondary coil and galvanometer.

In a preliminary trial, using an ordinary reflecting galvanometer, it was found that, instead of no deflection being observed, two kicks in opposite directions occurred when there was iron in the circuit. A new galvanometer with heavy needle is now being constructed to overcome this difficulty.

A null method of finding the ohm, by means of a differentially-wound heavy needle galvanometer, is suggested in the latter part of the note.

Prof. Ayrton pointed out that Prof. Foster's method does not require readings on a ballistic galvanometer, and mentioned that in practice it is greatly superior to those given in Maxwell and the ordinary text-books. The chief drawback is the necessity of having large condensers of accurately known capacity where large coefficients are concerned. A large number of experiments have been carried out at the Central Institution, by Mr. Sumpner, with very satisfactory results.

Prof. Adams concurred in Prof. Ayrton's statement regarding the difficulties in using Maxwell's methods in practice, and expressed his satisfaction with the great simplicity of Prof. Foster's method.

"*On the Determination of Coefficients of Mutual Induction by means of the Ballistic Galvanometer and Earth Inductor.*" By R. H. M. Bosanquet, M.A.

The methods described depend on two measurements of the throws of a ballistic galvanometer:—1st, that produced by the sudden rotation of a coil (the constants of which are accurately known) through 180° about a vertical axis; and 2nd, that produced by the mutual induction to be measured when a current of known strength is started in the primary circuit. The earth induction coil is permanently joined in series with the ballistic galvanometer and secondary coil, and the primary current measured by an absolute tangent galvanometer of the Helmholtz pattern.

If $Q_0$ and Q be the quantities of electricity which pass through the ballistic galvanometer in the two experiments, then—

$$Q_0 = \frac{2 N A H}{R},$$

where N A is the effective area of the inductor, and—

$$Q = \frac{M C}{R},$$

where $C = G H \tan \theta$. Hence—

$$\frac{Q}{Q_0} = \frac{M G \tan \theta}{2 N A} = \frac{\alpha}{\beta},$$

where $\alpha$ and $\beta$ are the throws of the ballistic galvanometer. From the above we get—

$$M = \frac{\alpha}{\beta} \frac{2 N A}{G \tan \theta}.$$

A modification to be used when M or R is very large is also described.

Numerical results obtained are given, from which it is inferred that Maxwell's formulæ for calculating the mutual induction of two circular coils cannot be applied where the distance between their central planes is at all comparable with their radii.

Experiments on an A gramme dynamo gave very irregular results when the currents were small, owing to the subpermanent magnetism of the machine.

Further uses of the method are suggested, such as the absolute determination of capacity and resistance.

Remarks on the subject were made by Prof. Carey Foster and Mr. Swinburne, and Prof. Ayrton replied to Mr. Swinburne's contention that Prof. Foster's method was not independent of observations of a ballistic galvanometer (since capacities are determined by their means), by pointing out that where accurate standards exist it is quite legitimate to base other absolute measurements on them.

Prof. Reinold then read an abstract of a paper on "*The Continuous Transition from the Liquid to the Gaseous State of Matter at all Temperatures.*" By Prof. W. Ramsay and Dr. Sydney Young.

The authors find the relation between pressure and temperature of gases and liquids at constant volume expressible by $p = b\,t - a$, where $b$ and $a$ are constants, and therefore conclude that the isochors (*i. e.*, curves connecting $p$ and $t$ for constant volume) are straight lines. At temperatures below the critical point the isotherm, during passage from the gaseous to the liquid state, is a serpentine curve intersected by the horizontal line of vapour-pressure corresponding with that temperature, the two areas between the curve and straight line being equal. By experiment and extrapolation the authors find the loci of the apices of the serpentine curves, corresponding with different temperatures, to intersect at the critical point.

The above results are proved for ether and carbonic dioxide, and the authors believe them to be true for all stable substances.

Prof. Rücker remarked that, if similar relations held for liquids and solids, the triple point of intersection would be of immense interest.

Prof. Perry, whilst regarding the results as of vast importance, thought the curves and calculations should be very carefully discussed before being finally accepted.

# NOTICES OF BOOKS.

*Year Book of Pharmacy*: comprising Abstracts of Papers relating to Pharmacy, Materia Medica, and Chemistry contributed to British and Foreign Journals, from July 1, 1885, to June 30, 1885; with the Transactions of the British Pharmaceutical Conference at the Twenty-third Annual Meeting, held at Birmingham, September, 1886. London: J. and A. Churchill.

The abstracts given in this goodly volume are arranged under the two heads of Chemistry and Materia Medica with Pharmacy. But the editors nevertheless find it difficult to draw a hard and fast boundary.

Thus we find in the second division an account of alkanet root and of its tinctorial principle anchusine, the whole being prefaced by the remark that the plant is "not used in pharmacy." Quillaja bark, once exclusively used in the tinctorial arts, has now found its way into medical use, on which account its place in the second section is perfectly

justifiable. Harmeline and its derivatives ought surely to have figured under the head of chemistry, the more as there is no mention of finding any pharmaceutical applications.

A paragraph by Du Moulin, quoted from the *Journal de Pharmacie*, confirms the opinion now becoming prevalent that copper can scarcely rank as a poison.

Salkowski's researches on the poisonous constituent of the mussel are chiefly quoted from *Chem. Centralblatt.* The poisonous specimens are said to yield a green alcoholic extract, while the extract of wholesome specimens is colourless. Will and Leymann's paper on the constituents of cochineal might have found a more appropriate place under chemistry.

The President, in his address, very appropriately asks —"Have we taken any steps to examine new and hitherto little-known drugs and to supply the most suitable formulæ for the preparation of the same before they get into the hands of the "mystery mongers" by whom they are brought to the notice of the medical profession?" He considers that the "proprietary preparations, for the most part 'factory made,' thrust upon the medical profession and unblushingly advertised, are sapping the foundations of true pharmacy and at the same time depriving the pharmacist of the legitimate practice of his calling." With the President's protest against this great and growing evil we can fully sympathise, and we hope that the Pharmaceutical Conference may devise some plan adequate to the occasion. But when Mr. Atkins speaks, apparently without disfavour, as far as general principles are concerned, of the poison Bill introduced by Lord Carlingford our sentiments are very different. We cannot protest too strongly, alike in the name of pure science and of the chemical arts, against all attempts to fetter the sale of the most indispensable reagents with red-tape formalities because, forsooth, they disagree with anyone who is foolish enough to swallow them. "Poison Bills" are something more than farcical in a country where professional criminals and members of dangerous societies can openly buy revolvers and ammunition.

## CORRESPONDENCE.

### TRANSPARENCY OF MOLTEN IRON.

*To the Editor of the Chemical News.*

Sir,—Some days ago I was present when a casting was made involving the pouring of several tons of molten cast-iron. The stream was very regular, and resembled a great waterfall. It was possible to see objects through the molten metal, which appeared to be of a yellowish colour, but tolerably transparent. Two gentlemen who were present were also convinced of the transparency of the metal. May I ask, through your columns, the opinion of those who have frequent opportunities of being present during the operation of casting, regarding this seeming transparency?—I am, &c.,

William Ramsay.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 4, January 24, 1887.

**Direct Fixation of the Gaseous Nitrogen of the Atmosphere by Arable Soils.** — M. Berthelot. — According to the author's experiments arable soil continually fixes free atmospheric nitrogen, even without any vegetation properly so-called. This gain cannot be ascribed to atmospheric supplies of nitrogenous compounds, whether gaseous or dissolved in rain-water. In the experiments where the rain water flowed away outside after having traversed the soil, the rain removed from the soil, in the shape of nitrates alone, more nitrogen than it had brought in the shape of ammonia and nitric acid taken together. Nevertheless the fixation of nitrogen was more considerable in earth exposed to the rain than in such as was under cover, doubtless by reason of the greater activity of the organisms which fix nitrogen by the circulation of air and water.

**Action of Carbon Tetrachloride upon Chlorochromic Acid and the Phosphates of Sesquioxide.**—H. Quantin.—The author has previously shown that carbon oxide splits up chlorochromic acid into green chromium sesquioxide and a sesquioxide of the same metal, and that an excess of chlorine determines its entire transformation into the violet chloride. It is the same with carbon chloride, the products being chromium sesquichloride, chlorocarbonic oxide, and free chlorine. Another interesting reaction occurs when carbon tetrachloride reacts upon oxy-salts. As an instance the author takes neutral ferric phosphate. If a current of the tetrachloride is passed over a boat containing this phosphate, heated below the decomposition-point of the tetrachloride, there are produced violet vapours. If these are passed through a column of potassium chloride heated to about 200° the ferric chloride is stopped in its passage, and in the cold parts of the tube following after the column of potassium chloride there is deposited a yellowish crystalline body of an irritating odour, which eagerly absorbs moisture. The excess of tetrachloride carries away a part of this body. The crystalline matter condensed in the tube is phosphorus perchloride.

**Preparation, Properties, and Constitution of Inosite.**—M. Maquenne.—Pure inosite is not attacked at its boiling-point by dilute acids and alkalies. It does not reduce cupropotassic liquor. It does not combine with sodium bisulphite, and is not attacked by sodium amalgam.

**Separation of Mono- and Di-isobutylamine by Means of Oxalic Ether.**—H. Malbot.—The general procedure recommended by MM. Duvillier and Busine enables us to obtain calcium mono- and di-isobutyloxamates which have not previously been produced. These two compounds are easily separated by crystallisation. By means of these two pure bodies we may obtain pure mono- and di-isobutylamine.

*Justus Liebig's Annalen der Chemie,* Vol. ccxxxvii., Part 1.

**Benzo-quinoncarbonic Acids.** — J. U. Nef. — The author studies the conversion of durol into durolquinone; its transformation into dinitrodurylic acid; the conversion of dinitrodurylic acid into durylic quinone and the conversion of dinitrodurylic acid into quinone tetracarbonic ethylester.

**Proportion of Carbonic Acid in the Atmosphere.**—R. Blochmann.—The author first reviews the earlier researches which, as he shows, gave excessive results. Up to 1870 it was supposed that air over continents contained, as a mean, 0·0004 volume of carbonic acid, or about one-fourth more than the true amount. The determinations of the earlier observers gradually approximated more and more closely to the truth. Thus, in 1827 Saussure found 5·1 volumes of carbonic acid in 10,000 vols. of air; in 1828 4·4; in 1829, 4·0; and 1830, 3·7. In like manner Schulze found, in his determinations from 1863 to 1864, a mean of 3·64 volumes per 10,000, whilst from 1868 to 1871 he obtained only 2·92. This fact proves that there are difficulties in the way of an exact quantitative determination of carbonic acid in the air, which the observer gradually overcomes

in virtue of experience and of increasing manipulative skill. The cause of the difficulties lies in the very nature of the problem. It is required to determine a magnitude which is only 0·0003 of the substance under examination. An error of only one-millionth as compared with the latter affects the value sought by one per cent. In every analytical operation a knowledge of the possible errors of observation is a necessary condition for the certain appreciation of the value of the result; a precise knowledge of the limits of error is here absolutely essential. In case of the determination of a relative magnitude, *e.g.* the difference of the carbonic acid by day and by night, a knowledge of the accidental errors is sufficient, as the constant errors disappear in the difference. But in ascertaining the mean proportion of carbonic acid in the air, *i.e.* an absolute magnitude, the constant error comes to the front. Synthetic attempts to check the sum of all errors of observation seem to have been made only twice, and these check experiments seem to have involved, in addition to the error of observation in the analysis, a further and opposite and almost equal error in the synthesis of the gaseous mixture. All the chemical methods used for the determination of carbonic acid depend on its absorption by alkalies or alkaline earths. Either they take into consideration the gaseous volume which has disappeared, or they determine directly the increase of weight of the absorbing agent, or they separate the carbonic acid as barium carbonate, or they ascertain by titration the reduced alkalinity of the absorptive liquid, or they re-liberate the carbonic acid after combination with an absorbent and measure its volume. All these methods resolve themselves into two groups, according as the volume of air operated on is bounded by the size of the apparatus or obtained by means of an aspirator. The former class embraces volumetric, gravimetric, and titrimetric processes. The volumetric method was first brought into use by A. v. Humboldt and was subsequently developed by Lewy, de Luna, Frankland, and Macagno. Even by the most exact eudiometric methods the carbonic acid of the atmosphere cannot be determined with certainty, and the conclusions which Lewy, Frankland, and Macagno drew from their researches cannot, therefore, be regarded as proven. Th. de Saussure is the only chemist who attempted to determine gravimetrically the acid in limited volume of air. His method was inconvenient, as it involved the use of flasks holding from 30 to 45 litres, previously exhausted of air, and involved certain sources of error. Dalton was the first to calculate the carbonic acid from the consumed absorbent. In this manner he executed, as far back as 1802, the first approximately accurate determination of the carbonic acid of the air. His mehod was forgotten, until revived in 1858 by Max v. Pettenkofer, without knowledge of Dalton's investigations. The aspiration methods likewise include direct weighing of the aspiration apparatus and titrimetric and volumetric determinations. The results as now ascertained are:—The average carbonic acid of our atmosphere is 0·00030 by volume. 2. The proportion of carbonic acid of the air over land and sea is in general the same. Over land the air contains by day 0·2 to 0·3 per 10,000 volumes less than by night. Over the sea a corresponding difference has not been recognised. 3. The fluctuations in the quantity of carbonic acid are generally within 1-10,000th part, about from 2·5 to 3·5 volumes for 10,000 vols. of air. 4. The influences of vegetation, of processes of decay in the soil, of the augmented consumption of fuel in cities, &c., are perceptible only in the immediate neighbourhood of such processes. Only volcanic actions have a measurable effect upon the proportion of carbonic acid in the air for great distances. 5. During fogs and when the sky is overcast and a calm prevails there is more carbonic acid than when the heavens are clear and the air in motion. As regards rain no definite regularities have been traced. The carbonic acid is sometimes increased in wet weather, sometimes diminished, and sometimes unchanged. 6. In towns the proportion of carbonic acid in the air is not everywhere alike, but depends on local circumstance. The difference between the average proportion of carbonic acid in the air of populous cities and in that of the open country is but slight, and in the cities, in which it has been established by simultaneous determinations, it does not exceed 0·2 to 0·3 vol. in 10,0000 vols. of air. The author has made experiments on the further development of the Dalton-Pettenkofer method, which, if performed as described in the text-books, always gives too high results. It requires, however, the fewest accessories and the shortest time. Errors may possibly arise during titration from the circumstance that the air of the laboratory is generally much richer in carbonic acid than the air outside. As the liquid has to be closely observed during titration, it appears certain that a part of the air expired, containing 1 m.g. carbonic acid per c.c., comes in contact with the baryta water during titration. The author, therefore, modifies the apparatus as shown in the six accompanying figures. For these illustrations, with which the execution of the process is intimately connected, we must refer to the original.

On Pipitzahoic Acid.—R. Anschütz and J. W. Leather.—This compound is a monobasic acid, but it belongs not to the carbon acids, but to the phenoles. From its splendid golden-yellow colour, considered in combination with the circumstance that it consists merely of carbon, hydrogen, and oxygen, it appeared to be a quinone, as it has been experimentally proved. Its constitution is analogous to that of oxythymoquinone.

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*Journal de Pharmacie et de Chemie.*
Series 5, Vol. xv., No. 2, January 15, 1887.

Two New Colours for Wines.—A. J. Ferreira de Silva.—An attempt has been lately made to introduce two new artificial colours to the Portuguese wine-growers. The one is a mixture of tropeoline O and methylene blue, and the other is rocceline red mixed with a violet and a blue matter, probably a rosaniline violet, and soluble indigo. Both these colours interfere with the preservation of wines, as they subside and carry down with them a part of the natural colour of the wines.

Vegetable Growths in Solution of Alkaloids.—L. Soubeiran.—The organisms in question are *Mucor mucedo*, *Aspergillus glaucus*, and *Penicillium glaucum*.

Certain Coloured Reactions of Titanic, Niobic, Tantalic, and Stannic Acids.—Lucien Lévy.—Already inserted.

Experimental Studies on the Action of Gases and Vapours Injurious to Health.—M. Lehmann.—The portion here inserted treats merely of hydrochloric acid and ammonia.

Studies on Digitaline.—Ph. Lafon.—The author does not admit that this poison accumulates in the animal economy. It seems to undergo a profound transformation in the circulation. Digitaline presents a relatively great resistance to physical and chemical agents, to ferments, and to putrefaction.

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## MISCELLANEOUS.

Messrs. Woodhouse and Rawson.—We have received from this firm the new edition of their illustrated catalogue and price list of electrical supplies, comprising incandescent lamps, electroliers, switches, safety fuses, electric bells, &c., &c. They inform us they make a point of keeping a stock of all small articles required by electrical engineers, a convenience which will be duly appreciated by those who have often lost much time waiting for the delivery of some article of comparatively small importance.

**Working Studentships.**—We are requested to announce that the Lords of the Committee of Council on Education have decided to make arrangements for the admission of a limited number of persons employed in industries in which Art is more or less concerned, to study in the South Kensington Museum, Library, and Schools, without the payment of any fees, for periods of from two to nine months, according to circumstances. Detailed rules with regard to these Working Studentships will be sent on application to the Department. Briefly, the conditions may be stated to be that the designer or workman for whom admission is sought shall show that he has sufficient power, in drawing and sketching, to be able to profit by the opportunities afforded; that he is actually engaged in some Art Industry, and that the proprietors of the Works in which he is engaged undertake to maintain him while he is studying at South Kensington. When admitted the working student will be set, under direction, to study in the Museum and Art Library from examples relating to the industry in which he is employed, and he will also receive instruction in drawing and designing in the Art School, suited, as far as may be, to his special case. This step has been taken with a view to render the Museum of more special and direct use to the country, and it is trusted that the valuable collection of examples of Applied Art which has now been brought together may thus be more fully appreciated and taken advantage of by the directors of industry in the country.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

**Sulphate of Ammonia.**—Is any book published that treats specially on the manufacture of sulphate of ammonia; and if so, where can it be obtained ?—H. W.

**Westphal Balance.**—I believe a description of the Westphal Balance appeared in the CHEMICAL NEWS some years ago. Can any of the readers refer the writer to it ?—CHEMIST.

## MEETINGS FOR THE WEEK.

MONDAY, 7th.—London Institution, 5.
—— Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "Building Materials," by W. Y. Dent, F.C.S.
—— Society of Chemical Industry, 8. "M. Hernick's System of Electrolytic Bleaching," by Messrs. Cross and Bevan. "Castner's Sodium Process," by J. Mactear. "A New Method of Elevating Liquids, specially applicable to Acids," by the same.
—— Royal Institution, 5. General Monthly Meeting.

TUESDAY, 8th.—Institution of Civil Engineers, 8.
—— Medical, 8.30. (Anniversary).
—— Photographic, 8.
—— Royal Institution, 3. "Function of Respiration,' by Prof. Arthur Gamgee, F.R.S.

WEDNESDAY, 9th.—Society of Arts, 8. "Railway Brakes," by William P. Marshall.
—— Geological, 8.
—— Pharmaceutical, 8.
—— Microscopical, 8.

THURSDAY, 10th.—Royal, 4 30.
—— Royal Society Club, 6.30.
—— Mathematical, 8.
—— Telegraph Engineers, 8.
—— Royal Institution, 3. "The Critics of the Age of Aune," by Edmund Gosse, M.A.

FRIDAY, 11th.—Royal Institution, 9. "Society in the Fourth Century," by The Ven. Archdeacon Farrar, M.A., D D., F.R.S.
—— Astronomical, 8.
—— Quekett Club, 8.

SATURDAY, 12th.—Royal Institution, 3. "Sound," by the Right Hon. Lord Rayleigh.
—— Physical, 3.

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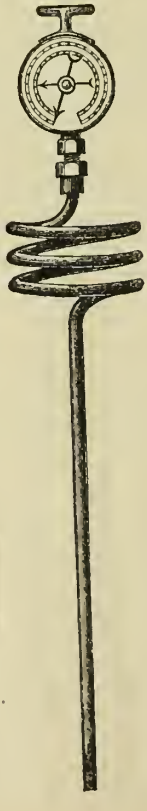
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THE CHEMICAL NEWS.

Vol. LV. No. 1424.

## ON RADIANT MATTER SPECTROSCOPY :— EXAMINATION OF THE RESIDUAL GLOW.*

By WILLIAM CROOKES, F.R.S., V.P.C.S.

The duration of phosphorescence after cessation of the exciting cause is known to vary within wide limits of time, from several hours in the case of the phosphorescent sulphides to a minute fraction of a second with uranium glass and sulphate of quinine. In my examinations of the phosphorescent earths glowing under the excitement of the induction discharge in vacuo, I have found very great differences in the duration of the residual glow. Some earths continue to phosphoresce for an hour or more after the current is turned off, while others cease to give out light the moment the current stops. Having succeeded in splitting up yttria into several simpler forms of matter differing in basic power,† and always seeking for further evidence of the separate identity of these bodies, I noticed occasionally that the residual glow was of a somewhat different colour to that it exhibited while the current was passing, and also that the spectrum of this residual glow seemed to show, as far as the faint light enabled me to make out, that some of the lines were missing. This pointed to another difference between the yttrium components, and with a view to examine the question more closely I devised an instrument similar to Becquerel's phosphoroscope, but acting electrically instead of by means of direct light.

The instrument, shown in Fig. 1, A and B, consists of an opaque disk, *a b c*, 20 inches in diameter, and pierced with 12 openings near the edge as shown. By means of a multiplying wheel, *d*, and band, *e f*, the disk can be set in rapid rotation. At each revolution a stationary object behind one of the apertures is alternately exposed and hidden twelve times. A commutator, *g* (shown enlarged at Fig. 1, B), forms part of the axis of the disk. The commutator is formed of a hollow cylinder of brass round a solid wooden cylinder. The brass is cut into two halves by a saw cut running diagonally to and fro round it, so as to form on each half of the cylinder twelve deeply cut teeth interlocking, and insulated from those on the opposing half cylinder by an air space about two millims. across. Only one half, *h h h*, of the cylinder is used, the other, *i i i*, being idle; it might have been cut away altogether were it not for some little use that it is in saving the rubbing-spring, *j*, from too great friction when passing rapidly over the serrated edge. To a block beneath the commutator are attached two springs. one, *k*, rubbing permanently against the continuous base of the serrated hemicylinder, *h h*, and the other, *j*, rubbing over the points of the teeth of *h h*. By connecting these springs with the wires from a battery it will be seen that rotation of the commutator produces alternate makes and breaks in the current. The spring, *j*, rubbing against the teeth is made with a little adjustment sideways, so that it can be set to touch the points of the teeth only, when the breaks will be much longer than the makes, or it can be set to rub near the base of the teeth, when the current will remain on for a much longer time and the intervals of no current will be very short. By means of a screw, *l l*, attached to the spring any desired ratio between the makes and the breaks can be obtained. The intermittent primary current is then carried to an induction coil, *m*, the secondary current from which passes through the vacuum tube, *n*, containing the earth under examination. When the commutator, the coil-break, and the position of the vacuum tube are in proper adjustment, no light is seen when looked at from the front if the wheel is turned slowly (supposing a substance like yttria is being examined), as the current does not begin till the tube is obscured by an intercepting segment, and it ends before the earth comes into view. When, however, the wheel is turned more quickly, the residual phosphorescence lasts long enough to bridge over the brief interval of time elapsing between the cessation of the spark and the entry of the earth into the field of view, and the yttria is seen to glow with a faint light, which becomes brighter as the speed of the wheel increases.

To count the revolutions, a projecting stud, *o*, is fastened to the rotating axis, and a piece of quill, *p*, is attached to the fixed support, so that at every revolution a click is produced. With a chronograph watch it is easy in this way to tell the time, to a tenth of a second, occupied in ten revolutions of the wheel.

Under ordinary circumstances it is almost impossible to detect any phosphorescence in an earth until the vacuum is so high that the line spectrum of the residual gas begins to get faint; otherwise the feeble glow of the phosphorescence is drowned by the greater brightness of the glowing gas. In this phosphoroscope, however, the light of glowing gas does not last an appreciable time, whilst that from the phosphorescent earth endures long enough for it to be caught in the instrument. By this means, therefore, I have been able to see the phosphorescence of yttria, for example, when the barometer gauge was 5 or 6 millims. below the barometer.

When the earth under examination in the phosphoroscope is yttria free from samaria, and the residual emitted light is examined in the spectroscope, not all the bands appear at the same speed of rotation. At a slow speed the double greenish-blue band of G$\beta$ (545) first comes into view, closely followed by the deep blue band of G$\alpha$ (482). This is followed, on increasing the speed, by the bright citron band of G$\delta$ (574), and at the highest speed the red band of G$\zeta$ (619) is with difficulty seen.

The following are measurements of the time of duration of the phosphorescences of the different constituents of yttrium. The wheel was first rotated slowly, until the first line visible in the spectroscope attached to the phosphoroscope appeared; the speed was counted, and it was then increased until the line next visible was seen. In this way the minimum speed of revolution necessary to bring each line into view was obtained, and from these data the duration of phosphorescence for each constituent of yttria was calculated. The time in the following table represents in decimals of a second the time elapsing between the cessation of the induction discharge and the visibility of the residual glow of the earth :—

| | | |
|---|---|---|
| At 0·0035 sec. | interval | the green and blue lines of G$\beta$ and G$\alpha$ begin to be visible. |
| At 0·0032 ,, | ,, | the citron line of G$\delta$ begins to be visible. |
| At 0·00175 ,, | ,, | the deep red line of G$\zeta$ (647) is just visible. |
| At 0·00125 ,, | ,, | the line of G$\delta$ is almost as bright as that of G$\beta$, and the red line of G$\eta$ is visible. |
| At 0·000875,, | ,, | the highest speed the instrument could be revolved with accuracy, all the whole of the lines usually seen in the yttria spectrum could be seen of nearly their usual brightness. |

I have already recorded* that phosphate of yttria, when phosphoresced in vacuo, gives the green lines very strongly whilst the citron band is hazy and faint. The same tube of yttric phosphate was now examined in the phosphoroscope. The green lines of G$\beta$ soon showed themselves on setting the wheel into rapid rotation, but I

* A Paper read before the Royal Society, Feb. 17, 1887.
† *Roy. Soc. Proc.*, vol. xl., pp. 502—509, June 10th, 1886.

* *Phil. Trans.*, Part 3, 1883, pp. 914-916.

was unable to detect the citron band of Gδ even at a very high speed.

The effect of calcium on the phosphorescence of yttria and samaria has been frequently referred to in my previous papers. It may save time if I summarise the results here. About 1 per cent of lime added to a badly phosphorescing body containing yttrium or samarium always causes it to phosphoresce well. It diminishes the sharpness of the citron line of Gδ but increases its brightness. It also renders the deep blue line of Gα extremely bright. The green lines of Gβ are diminished in brightness. Lime also brings out the phosphorescence of samarium, although by itself, or in the presence of a small quantity of yttrium, samarium scarcely phosphoresces at all.

In the phosphoroscope the action of lime on yttrium is seen to entirely alter the order of visibility of the constituents of yttrium. In a mixture of equal parts yttrium and calcium, the citron Gδ line is the first to be seen, then comes the Gα blue line, then the Gβ green line, and finally the Gη red line. This may, I think, be explained somewhat as follows:—Calcium sulphate has a long residual phosphorescence, whilst yttrium sulphate has a comparatively short residual phosphorescence. Now with

Fig. 1, A.

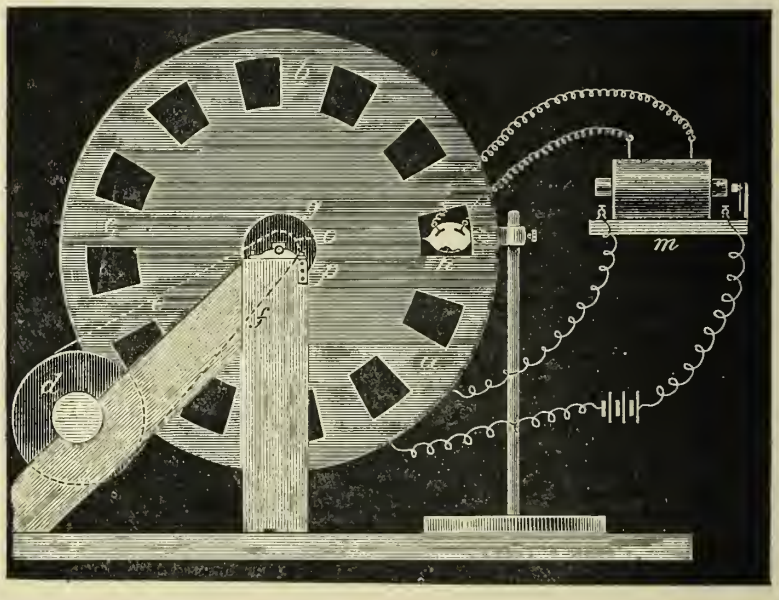
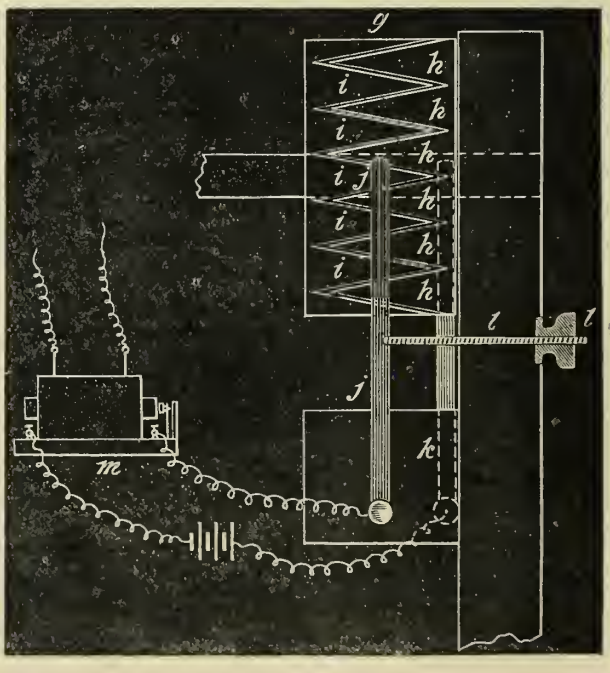



Fig. 2, B.



yttrium, although the green phosphorescence of Gβ lasts longest, it does not last nearly so long as that of calcium sulphate. The long residual vibrations of the calcium compound induce, in a mixture of calcium and yttrium, phosphorescence in those yttric molecules (Gδ) whose vibrations it can assist, in advance of those (Gβ) to which it is antagonistic; the line of Gδ therefore appears earlier in the phosphoroscope than that of Gβ, although were calcium not present the line of Gβ would appear first.

Experiments were now tried with definite mixtures of yttria and lime as ignited sulphates, to see where the special influence of lime on Gδ ceased.

| | | |
|---|---|---|
| Yttrium 97½% | Calcium 2½% | Order of appearance in the phosphoroscope.—Gβ, Gα, Gδ, and Gη. The citron line of Gδ is only to be seen at a high speed, and is then very faint. |
| Yttrium 95% | Calcium 5% | Order of appearance in the phosphoro scope. — Gα, Gβ, and Gδ (citron and blue) together, and lastly Gη (red). At a very high speed the green lines of Gβ become far more luminous than any other line. |
| Yttrium 90% | Calcium 10% | Order of appearance.—Gδ and Gα together, then Gβ, and lastly Gη. |
| Yttrium 80% | Calcium 20% | Order of appearance.—Gδ and Gα simultaneously, then Gβ, and lastly Gη. The residual phosphorescence lasts for 30 seconds after the current stops. The light of this residual glow is entirely that of Gδ. The line of Gβ comes into view at an interval of 0·0045 second. At 0·00175 second the line of Gη is just visible. |
| Yttrium 60% | Calcium 40% | Order of appearance.—Gδ and Gα together, then Gβ and Gη together. |
| ,, 50 | ,, 50 | |
| ,, 40 | ,, 60 | |
| Yttrium 30% | Calcium 70% | Order of appearance:—Gδ, Gα, Gβ. |
| ,, 10 | ,, 90 | |
| ,, 5 | ,, 95 | |
| Yttrium 1% | Calcium 99% | Order of appearance:—Gδ, Gα, the green lines of Gβ could not be seen in the phosphoroscope, they would probably be obliterated by the stronger green of the continuous spectrum given by the calcium. |

The action of barium on yttrium was now tried. The following mixtures (as ignited sulphates) were made:—

| | | |
|---|---|---|
| Yttrium 95% | Barium 5% | In the phosphoroscope, the Gβ line appears earliest, but the blue Gα line is the next to be seen, whilst the red line of Gη is the latest in appearing. As the percentage of yttrium increases the blue line more and more overtakes the red and increases in brightness. |
| ,, 90 | ,, 10 | |
| ,, 80 | ,, 20 | |
| Yttrium 70% | Barium 30% | Spectrum similar to the above. As the percentage of yttrium increases the spectrum grows brighter. In the phosphoroscope the earliest line to appear is the Gβ green, then the Gη red, and next closely following it the Gα blue. |
| ,, 60 | ,, 40 | |
| ,, 50 | ,, 50 | |
| ,, 40 | ,, 60 | |
| ,, 30 | ,, 70 | |
| ,, 25 | ,, 75 | |
| Yttrium 20% | Barium 80% | In the radiant matter tube all these mixtures give similar spectra. The Gβ green is a little brighter and the Gδ citron is a little fainter than in the corresponding mixtures of yttrium and calcium, but the whole of the yttrium lines are seen. In the phosphoroscope the Gβ green is the first to appear, then the Gη red. The Gδ citron is not visible at any speed. |
| ,, 15 | ,, 85 | |
| ,, 10 | ,, 90 | |
| ,, 5 | ,, 95 | |
| Yttrium 1% | Barium 99% | Red line of Gη is much brighter; Gδ is very faint, and the green of Gβ is stronger. In the phosphoroscope the order of appearance is,—first the line of Gβ, then the red line of Gη. |
| Yttrium 0·5% | Barium 99·5% | Phosphoresces with difficulty, of a light blue colour, but turns brick-red in the focus of the pole. Spectrum very faint. Order of appearance to phosphoroscope:—Gβ first; the others too faint to be seen. |

The next experiments were tried with strontium, to see what modification the addition of this body to yttrium would produce. The following mixtures of ignited sulphates were experimented with:—

| | | |
|---|---|---|
| Yttrium 95% | Strontium 5% | A very good yttrium spectrum. In the phosphoroscope the order of appearance is,—First the green of Gβ, then the Gα blue, lastly, the Gη red. No Gδ citron line could be seen. |
| Yttrium 80% | Strontium 20% | In the phosphoroscope the green of Gβ is very prominent at a low speed, standing out sharply against a black background. With a higher velocity the Gα and Gη lines come into view. |
| Yttrium 60% | Strontium 40% | The ordinary spectrum of this and the neighbouring mixtures is very rich in the citron line of Gδ, but I entirely fail to see a trace of this line in the phosphoroscope at any speed. The line of Gβ is the first to come, then the blue line of Gα. |
| ,, 40% | ,, 60% | |

| | | |
|---|---|---|
| Yttrium 35% | Strontium 65% | At about this point a change comes over the appearance in the phosphoroscope. The blue line of G$\alpha$ is now the earliest to appear, and it is followed by the G$\eta$ red and G$\beta$ green. No G$\delta$ line is seen. |
| Yttrium 25% | Strontium 75% | These mixtures are very similar to each other in the phosphoroscope. The line of G$\alpha$ comes first, next the G$\eta$ line, then G$\beta$ line. No G$\delta$ citron line has been seen in any of these mixtures. |
| ,, 15 | ,, 85 | |
| ,, 5 | ,, 95 | |
| ,, 0'5 | ,, 99'5 | |

In a paper read before the Royal Society, June 18th, 1885,* I described the phosphorescent spectrum given by a mixture of 61 parts of yttrium and 39 parts of samarium,

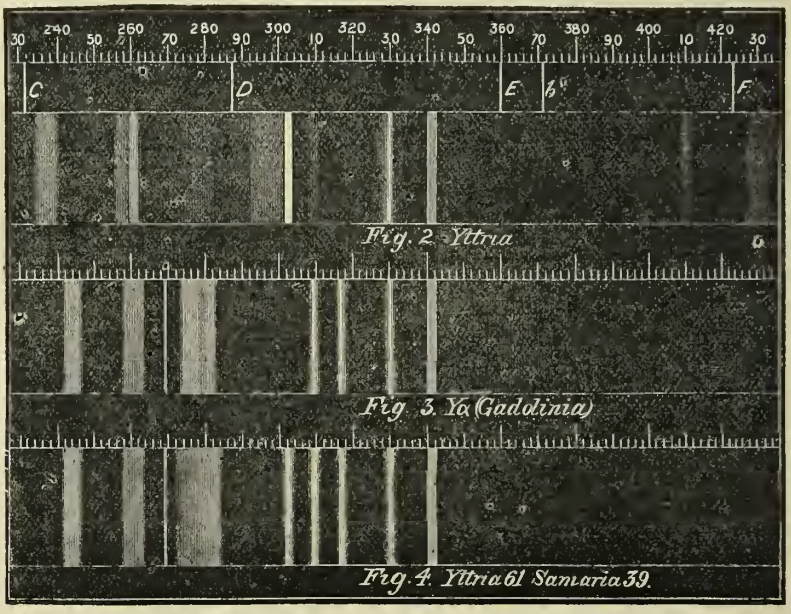



*Fig. 2. Yttria*

*Fig. 3. Yα (Gadolinia)*

*Fig. 4. Yttria 61 Samaria 39.*

and illustrated it by a coloured lithograph. Also in a paper read before the Royal Society, February 25th, 1886,† I described and figured the phosphorescent spectrum of an earth obtained in the fractionation of yttria which was identical, chemically and spectroscopically, with an earth discovered by M. de Marignac, and provisionally called by him Y$\alpha$. I repeat here these spectra, with the spectrum of yttrium added for comparison. Omitting minor details, it is seen that the Y$\alpha$ spectrum is identical with that of the mixture yttrium 61 samarium 39, with one important exception—the citron line of G$\delta$ in the former spectrum is absent in the latter. Could I by any means remove G$\delta$ from the mixture of yttrium and samarium the residue would be Y$\alpha$. I have little doubt that this will soon be accomplished, but in the meantime the phosphoroscope enables us to remove the line of G$\delta$ from the mixture. It is only necessary to add strontium to a suitable mixture of yttrium and samarium and view the phosphorescing mixture in the instrument when the wheel is rotating rapidly, to obtain a spectrum which is indistinguishable from that of Y$\alpha$.

(To be continued.)

* *Phil. Trans.*, Part 2, 1885, p. 716.
† *Roy. Soc. Proc.*, vol. xl., p. 236.

## RELATION OF THE CHEMICAL CONSTITUTION OF INORGANIC COMPOUNDS TO THEIR PHYSIOLOGICAL ACTION.

By Dr. JAMES BLAKE.

THE first fact I observed connecting the biological action of inorganic substances with their chemical constitution, was that when introduced directly into the blood their action was dependent on the electro-positive element of the compound, and was but slightly modified by the acid with which it was combined. I published this fact in a paper read before the Academie des Sciences, at Paris, in 1839.

The next generalisation that I arrived at was that the biological action of the compounds of the elements was connected with their isomorphous relations, the compounds of the elements in the same isomorphous group giving rise to analogous biological reaction. (This relationship was suggested to me by the late Prof. Graham, in whose laboratory I was working at the time, on my calling his attention to the fact that the salts of silver, when introduced into the blood, gave rise to the same reactions as the salts of soda.)

On working out this hypothesis, experiments with the salts of the magnesian and the baryta groups of metals fully confirmed the truth of Graham's supposition. These results were published in a paper read before the Royal Society in January, 1841, and the experimental investigation of the biological action of compounds of more than forty of the elements has since confirmed them, the salts of potash, however, forming an exception.

In a paper read before the Academie des Sciences, at Paris, in 1839, I had already shown that when introduced directly into the blood the biological action of a salt is determined by the electro-positive element, the sulphates, nitrates, arseniates, phosphates, chlorides, &c., of the same base causing the same biological actions.† This is evidently a corollary of the fact that connects the biological action of a substance with isomorphism, as these

* Paper read before the University College Chemical and Physical Society, on February 3rd, 1887.
† It would seem that in the nitrites, and in the pyrophosphates and pyrovanadates, the acid exerts some influence in intensifying the biological action of the base.

isomorphous relations are determined by the electro-positive element of the compound.

In a paper read before the Californian Academy of Sciences, in 1873, I published the fact that in the same isomorphous group the intensity of biological action is a function of the atomic weight; the higher the atomic weight of an element, in the same isomorphous group, the smaller the quantity required to cause the same amount of biological action.

When injected into the jugular vein, the first sensitive tissue with which the reagent is brought into contact is the blood-vessels in the lungs. These blood-vessels are a most delicate test for the alkaline elements, whose presence in the blood causes them to contract, and when in sufficient quantity they completely arrest the passage of the blood through the lungs. This reaction is caused not only by the more characteristic elements,—lithium, sodium, rubidium, cæsium, and thallium,—but also by those elements which are connected with them by isomorphous relations,—silver, gold, and lead. So delicate is this test that the presence in the blood of 1-50,000th part of its weight of a salt of gold can be readily detected,—not indeed as gold, but as a substance with chemical properties analogous to those of the alkaline metals.

There are other elements which cause contraction of the pulmonary vessels, yet none of the salts that have been used give rise to the same action on the lung tissue.

The next organ to which our reagents are applied is the heart, for, although they have been already in contact with the internal surface of the organ it is only after having passed the left ventricle and circulated through its tissues that any reaction takes place. The whole of the alkaline elements and those related to them keep up its contractions after respiration has ceased,—the lithia salts for from twelve to fifteen minutes, the rubidium salts for thirty-one minutes, and the gold salts for many hours after death, the presence of 1-50,000th the weight of the blood of a gold salt producing this reaction; the whole of the salts of the magnesia group and the baryta group destroy its irritability, suddenly arresting its action a few seconds after they have been introduced into the veins. The oxygen and hydrogen compounds of the chlorine group have the curious effect of keeping up the irritability of the ventricles after that of the auricles has ceased. After having passed through the heart the reagent is brought into contact with the arteries that carry it over the whole body. These vessels are affected by some of these inorganic substances in the same way as are the lung arteries by the soda group. The salts of the platinum group cause them to contract, although they do not affect the lung-vessels, whilst the salts of the soda group which act on the lung arteries pass through the systemic arteries without affecting them. The salts of the alumina group contract both the systemic and pulmonary arteries, whilst the salts of the magnesian group affect neither.*

The next important organs with which our reagents are brought into contact are the nerve-centres. In the medulla oblongata are various centres regulating distinct functions, although hardly to be distinguished anatomically. Amongst these are the respiratory centre, the vasometer centre, the vomiting centre, &c. The salts of the platinum group exert a marked action on the respiratory centre, the salts of the magnesian group react on the vomiting centre, the thorium salts on the vasometer centre, and the baryta group on the cord, whilst the salts of the more typical alkaline metals have no action on any part of the nervous system. The salts of the magnesian group and the platinum group interfere with the coagulation of the blood. These elements which form connecting-links between two isomorphous groups cause biological reactions which are common to the two groups,—the salts of lead, for example, acting on the lung-vessels as do the alkaline elements, and on the spinal cord in the same manner as the baryta group of salts.

When an element forms two classes of salts the biological action of each class is perfectly distinct, each producing the reactions characteristic of the isomorphous group to which it belongs. Thus the ferrous salts agree with the other members of the magnesian group, and the ferric salts with the other members of the aluminum group in their biological action. If we now consider the relation between atomic weight and biological action, we shall find this is not shown by any effect on the general biological action of the compound, but by the fact that in the same isomorphous group the *intensity* of biological action is increased with the atomic weight; the greater the atomic weight of an element the smaller the quantity required to cause the same amount of biological action. This connection is not so marked as that which exists between the isomorphous relations of the elements and their general biological action, slight modifications in chemical properties apparently exerting a greater influence on this quantitative reaction than on the qualitative, nor is it found at all among the more electro-negative elements.*

The following figures show the quantity expressed as oxide of the elements, with the highest and lowest atomic weights, in each isomorphous group, that are required per kilo. of animal to cause the same amount of biological action:—

| | | | |
|---|---|---|---|
| Lithium .. .. | 0·420 | Magnesia .. | 0·031 |
| Thallium .. .. | 0·023 | Cadmium .. | 0·026 |
| Lime .. .. | 0·220 | Beryllium .. | 0·023 |
| Baryta .. .. | 0·025 | Ferric oxide .. | 0·003 |

Such is a summary of the facts that have been ascertained in testing the biological action of compounds of more than forty of the elements, by introducing them directly into the blood of living animals.†

As to the nature of these reactions—whether they are analogous to any that take place between other forms of matter, or whether they constitute a class apart which has yet to be recognised—it would at present be premature to give an opinion. There are, however, some considerations which would lead us to connect them with contact relations, so that the changes that are constantly going on in the living tissues, and on which the functions of each organ depend, are modified in different directions by mere contact with these inorganic substances. As our living reagents are substances of high molecular weight, and in a state of constant change, they are of all forms of matter most likely to be the seat of contact reactions, and will, I think, be useful in elucidating this branch of chemistry. Experiments by Dujardin, Beaumetz, and Audigé render it highly probable that the connection between chemical properties and biological action that has been proved with inorganic substances is also to be found in the carbon compounds. They show that all the alcohols in the same series cause analogous biological reactions, and also that, as in the different isomorphous groups, the toxic power increases with the atomic weight. Schmerdehery has also shown that the biological action of the ether salts is dependent on the electro-positive molecule, and is but slightly influenced by the acid with which it is combined.

Should these observations be generalised, living matter will prove an important reagent in determining the chemical constitution of the carbon compounds.

* These effects both on the systemic and pulmonary arteries can be readily observed by means of a manometer.

* It should be remembered that our knowledge of the connection between the general chemical properties of the elements and isomorphism is still imperfect,—in fact, has advanced but little beyond the point where Mitscherlich left it seventy years ago. Our classification, too, of the elements in isomorphous groups implies nothing more than a general family resemblance between the elements in the same group, admitting undoubtedly of considerable modifications in their chemical properties.

† Details of these experiments will be found in *Proc. Roy. Soc.*, vol. v., 1841; *Reports of Brit. Assoc.* for 1843, 1845, 1846; *Journal of Physiology*, vol. v.

# INVESTIGATION ON THE ATOMIC WEIGHT OF TUNGSTEN.

By JOHN WADDELL, Ph.D. (Heidelberg), D.Sc. (Edin.).

(Concluded from p. 102).

THE fractionations were made in the following manner:—To the boiling solution in a porcelain basin 20 to 30 c.c. hydrochloric acid, 1·135 sp. gr., were added, and the boiling continued till considerable precipitate appeared. The contents of the basin were then removed to a large beaker (about 2 litres), and hot water added (if necessary) to fill the beaker. When the tungstic acid had settled, the clear supernatant liquid was decanted and the precipitate washed twice by decantation. Further washing was impossible, unless with addition of hydrochloric acid, for the tungstic acid did not settle, but made the liquid milky. Sometimes the acid necessary for the subsequent precipitation was added to the last washing. The decantations were evaporated to the bulk of the original solution, and if the requisite acid had not before been added it was now poured in and another precipitation obtained.

In this way eleven fractionations were prepared of these: the first was dark green, those following as far as the seventh were light yellow, while the remaining ones were dirty green and not so finely divided as the preceding. The colour of the first precipitate was probably due to want of complete oxidation by the current of air passed through the liquid, while the condition of the final fractionations was doubtless caused by the fact that, in order to get a reasonable quantity of the tungstic acid, evaporation to small bulk was required. The tartaric acid probably under these circumstances exercised a reducing action, while the continued boiling promoted coagulation.

For the atomic weight determinations three of these fractionations were purified,—viz., III., X., and VII. A description of the treatment of III. will show the general method. The precipitate was washed several times by decantation, and then repeatedly on a filter with very dilute (say 3 per cent) hydrochloric acid. It was afterwards dissolved in ammonia, filtered from the very trifling residue, and re-precipitated by hydrochloric acid (the best method is by pouring the boiling solution into excess of hydrochloric acid). This precipitate was again washed by decantation and on the filter till the washings yielded no residue on evaporation, and a test portion of the precipitate gave only a slight indication of sodium by the spectroscope.

The hydrochloric acid was freed from a possible trace of arsenic by digestion with copper-foil, and was afterwards three times distilled. The ammonia was re-distilled from baryta. Both it and the acid were proved to be free of anything leaving a solid residue on evaporation. The precipitate was dried, powdered, and heated to redness in a current of air, in order to get rid of the last traces of hydrochloric acid and ammonium chloride, and to ensure complete oxidation. This ignition lasted several hours. The tungstic acid thus obtained was quite uniform in appearance, and of a beautiful pale canary-yellow colour.

Some of this tungstic acid was afterwards reduced in a current of hydrogen (purified by passing through large U-tubes containing pumice moistened respectively with lead nitrate, silver nitrate, caustic potash, and strong sulphuric acid). Care was taken to increase the temperature gradually, in order to prevent the tungstic acid from volatilising before reduction. The temperature was finally raised to the highest attainable by a strong blast in Fletcher's furnace. The material before and after reduction was weighed in a porcelain boat enclosed in a glass weighing tube, and counterbalanced by a similar tube containing an empty boat. In order to see whether volatilisation had taken place, the porcelain tube in which the substance had been heated was wiped out with cotton-wool, and when the wool remained perfectly clean it was assumed that there had been no volatilisation. Several experiments showed that very slight amounts of volatilisation were capable of being thus detected. At the highest temperature of the furnace there was danger of the boat fusing to the tube unless protected in some way. The plan adopted was to wind a couple of pieces of platinum wire about the boat. Contact with the tube was thus prevented.

I assumed, as has always been done, that hydrogen reduces tungstic acid to metallic tungsten. I proved that no hydrogen is occluded by weighing one specimen of the metal obtained as above, and afterwards heating it to redness under diminished pressure and again weighing. The weight was constant. The fraction X., to which XI. was added, was subjected to the same treatment as III., but never attained the same stage of apparent purity. During the reduction, too, a slight volatilisation occurred. I therefore purified VII. with quite satisfactory results, and the atomic weight determination was only slightly below those obtained with III. Subjoined is a table of determinations:—

| Fraction. | $WO_3$ taken. | W left. | $O_3$ lost. | Atomic weight. | Remarks. |
|---|---|---|---|---|---|
| III. | *1·4006 | 1·1115 | 0·2891 | 184·55 | No volatilisa- |
| | 0·9900 | 0·7855 | 0·2045 | 184·37 | [tion. |
| | 1·1479 | 0·9110 | 0·2369 | 184·59 | |
| VII. | 0·9894 | 0·7847 | 0·2047 | 184·00 | [isation. |
| X. | 4·5639 | 3·6201 | 0·9438 | 183·67 | Slight volatil- |

The mean of the atomic weights as determined in III. is 184·5, if oxygen be regarded as 16. If O = 15·96, then W = 184·04. The estimation in VII. so nearly agreed with the others that it was not thought necessary to make any further determinations.

I think there can be no doubt that the commonly accepted atomic weight is practically correct. It is useless to attempt to be more accurate while the atomic weights of such elements as oxygen are open to dispute.

I made some determinations of atomic weights in precipitates from tungstate which had not been freed from molybdenum. The first fractionation was most carefully examined. It might naturally be expected to contain the greater portion of the molybdic acid, in which case a low result was to be looked for, not only because the atomic weight of molybdenum is only about half that of tungsten, but also because the experimental error of volatilisation is more difficult to avoid. A very slight volatilisation was observed, and as a mean of four experiments the number 183·68 was obtained. These determinations may be considered confirmatory of the more accurate ones, for the variation was just in the direction to be expected. Of course by themselves they are of little value.

The precipitates obtained by fractionation gave practically concordant results, and hence pointed to absence of impurity. I, however, tested independently for silica by fusing with sulphate. A test experiment proved that the sodium salt acted in the same way as the potassium salt. To the mixed sodium tungstate and carbonate which had been used for my investigations I added a few drops of strong sulphuric acid, and fused as described in the Appendix. No silica was found.

I made two determinations of specific gravity,—one of metal not specially freed from molybdenum, another of a portion of III. which was considered pure. The numbers obtained were 18·25 and 18·77. These so nearly corresponded with the determinations of other investigators that I did not pursue the matter further. The second determination is doubtless the more accurate.

The result of my work has therefore been confirmatory of the accuracy of previous investigations. So far as I am aware, the method of operation has not been applied to tungsten before, and the agreement affords a trustworthy corroboration.

* Weights are in grammes.

### Appendix.

The separation of silica and tungstic acid by fusion with potassium hydrogen sulphate is troublesome unless attention be paid to some important details. About equal weights of the sulphate and mixture of tungstic acid and silica are fused till the evolution of sulphuric anhydride almost ceases. The fused mass should then be limpid and flow quietly. This is the stage when the acid sulphate, $KHSO_4$, is changed to the compound $K_2S_2O_7$. The silica should be seen floating about in the fused mass. The crucible having been cooled, the fused mass should be powdered and added to boiling water. After further boiling, the undissolved material should be allowed to settle, and the supernatant liquid decanted through a filter. Fresh water is added to the residue, and again boiled and decanted. Further washing with pure water will probably be found impracticable, because the precipitate tends to run through the filter. Dilute ammonium carbonate should then be employed. This dissolves the remaining tungstate, as well as tungstic acid, the silica being left unattacked. After the precipitate is removed to the filter it should be washed a number of times with hot water containing ammonium carbonate.

As the last traces of tungsten are difficult to wash out, it is probably necessary for exact quantitative separation to dry the precipitate and fuse again with a little acid sulphate. In quantitative estimation, also, it will not be easy to powder the fused mass without loss. It is therefore best, under such circumstances, to remove the mass in lumps and digest with water for a longer time. The operation is slower, but otherwise equally good.

To dissolve tungstic acid in ammonia it is best to have the substance in a bottle. Then add a moderately strong but not saturated solution of ammonia, shake violently for several minutes, allow to settle, and decant the most of the supernatant liquid; add water to the remainder and shake again. Decant as before, and repeat the process if necessary. It may then be necessary to add a little more ammonia, but in most cases the tungstic acid will be entirely dissolved. It is of little, if any, advantage to use hot water. — *American Chemical Journal*, August, 1886, p. 280.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, March 3rd, 1887.*

Dr. Hugo Müller, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. James Warne Chenhall, Churston, near Brixham, Devon; George Collar, B.A., 28, Sterndale Road, West Kensington Park, W.; Hugh Gordon, 3, Courtfield Gardens; David Lloyd Howard, Rectory Manor, Walthamstow; Edward Rawlins, Burley Road, Leeds; Louis H. Schubart, 201, West 125th Street, New York.

The following were elected Fellows of the Society:—Messrs. Cecil Howard Cribb, Leonard Dobbin, Joseph F. Geisler, Edgar Hall, Alexander Hay, Thomas A. Hedley, John S. Jackson, George McGowan, Gerald T. Moody, Joseph W. O'Connor, Henry D. Richmond, Arthur H. F. Ruppel, W. Scrutton, Henry Lloyd Snape, B.Sc., Arthur Stanley, Henry Wallis.

The following papers were read:—

18. "*Tartaric and Racemic Acids, and the Magnetic Rotatory Power of their Ethyl Salts.*" By W. H. Perkin, Ph.D., F.R.S.

The author has very carefully determined and compared certain physical properties of the diethylic salts of ordinary tartaric and racemic acids, prepared by the usual method by saturating the alcoholic solution of the acid with hydrogen chloride. Both boil at 232° to 233° (corr.) under a pressure of 197 m.m. They have the same relative density, viz.:—

Diethylic tartrate .. $d\frac{15^\circ}{15^\circ} = 1{\cdot}20972$ $d\frac{25^\circ}{25^\circ} = 1{\cdot}20189$.

,, racemate . $d\frac{15^\circ}{15^\circ} = 1{\cdot}20983$ $d\frac{25^\circ}{25^\circ} = 1{\cdot}20214$.

They have also the same mean molecular magnetic rotatory power, viz.:—

Diethylic tartrate at 14·8° = 8·766
,, racemate at 15·5° = 8·759.

It may therefore be concluded that the racemate is a mixture of the two tartrates.

Racemic is distinguished from tartaric acid by crystallising with 1 mol. proportion of water; the author finds that silver racemate, like the tartrate, is anhydrous. In preparing silver tartrate he obtained an acid salt,—

$$C_4H_5AgO_6{\cdot}H_2O,$$

crystallising in well-defined monoclinic prisms, measurements of which by Prof. Haushofer are given. An acid silver racemate appears also to exist, but is much less soluble than the tartrate, and the crystals are small.

The relative densities of aqueous solutions of the two acids were determined, using (*a*) a solution containing 8·333 per cent, and (*b*) a solution containing 25 per cent, the latter being supersaturated in the case of racemic acid: the results are—

| | (*a*) | (*b*) |
|---|---|---|
| Tartaric acid solution | $d\frac{15^\circ}{15^\circ} = 1{\cdot}03703$ | $d\frac{15{\cdot}3^\circ}{15^\circ} = 1{\cdot}12346$. |
| Racemic acid solution | $d\frac{15^\circ}{15^\circ} = 1{\cdot}03712$ | $d\frac{15{\cdot}3^\circ}{15^\circ} = 1{\cdot}12398$. |

The relative densities of the solid acids were also determined:—

Racemic acid, $C_4H_6O_6{\cdot}H_2O$ .. $d\frac{7^\circ}{4^\circ} = 1{\cdot}6873$.

,, ,, dehydrated .. .. = 1·7782.
Tartaric acid .. .. .. .. .. = 1·7594.

These results, the author considers, point to the conclusion that on dissolving in water racemic acid separates into the two tartaric acids, only a small quantity remaining unchanged. He is of opinion that the water is present in crystallised racemic acid as such; and he finds that, if the hydrated acid be crystallised from absolute alcohol, well-defined anhydrous crystals are obtained much less soluble than tartaric acid in alcohol.

19. "*Anhydracetonebenzil.*" By Francis R. Japp, F.R.S., and Cosmo Innes Burton, B.Sc.

*Anhydracetonebenzil* (formerly *dehydracetonebenzil*), $C_{17}H_{14}O_2$, was originally prepared by Japp and Miller (*Trans.*, 1885, 27) by the condensation of benzil with acetone under the influence of caustic potash; they concluded that it contained a closed chain formed by the interaction of the acetone with the lateral chain of the benzil. The authors adduce further evidence in support of this view.

Anhydracetonebenzil reacts with phenylhydrazine, forming the compound $C_{17}H_{14}O(N_2H{\cdot}C_6H_5)$ (slender, yellow needles, melting at 197°), which is not altered by heating with excess of phenylhydrazine.

By boiling anhydracetonebenzil for a few minutes with iodhydric acid it is deprived of an atom of oxygen, and yields a compound, $C_{17}H_{14}O$ (colourless prisms from alcohol, m.p. 110°). This reacts with phenylhydrazine, forming $C_{17}H_{14}(N_2H{\cdot}C_6H_5)$, which crystallises from alcohol in rosettes of short yellow needles, melting with decomposition at 170° to 180°.

Fuming iodhydric acid and amorphous phosphorus at 130° convert anhydracetonebenzil into a hydrocarbon,

$C_{17}H_{18}$, which crystallises from alcohol in colourless, long, flat needles, melting at 47°, and distilling under ordinary pressures with partial decomposition at 305° (uncorr.). The authors regard this hydrocarbon either as diphenylpentamethylene (1, 2), or as phenylbenzyltetramethylene (1, 1). It is not reduced to $C_{17}H_{20}$ by the action of the hydriodic acid at a higher temperature, as it would be if it were an unsaturated open-chain compound—diphenylamylene.

By reduction with tin and hydrochloric acid in alcoholic solution, anhydracetonebenzil is converted into a compound, $C_{34}H_{34}O_2$, very sparingly soluble in alcohol, from which it crystallises in lustrous, minute rhomboidal plates, melting at 187° to 188°.

When boiled with sulphuric acid diluted with twice its volume of water, 2 mols. of anhydracetonebenzil part with 2 mols. of water, and unite, forming a compound, $C_{34}H_{24}O_2$, which crystallises from benzene in two forms—one with, the other without, benzene of crystallisation. This substance melts with decomposition at 195° to 200°, evolving exactly one molecular proportion of carbonic oxide, according to the equation—

$$C_{34}H_{24}O_2 = C_{33}H_{24}O + CO.$$

The compound $C_{33}H_{24}O$ crystallises from benzene in small plates of the formula $C_{33}H_{24}O,C_6H_6$, which, after expelling the benzene, melt at 162° to 163°. It reacts with phenylhydrazine, yielding $C_{33}H_{24}(N_2H{\cdot}C_6H_5)$ (pale yellow, slender needles, very sparingly soluble in alcohol, m.p. 250°. In this respect it differs from its parent compound, $C_{34}H_{24}O_2$, which does not react with phenylhydrazine.

Anhydracetonebenzil, when treated with concentrated alcoholic chlorhydric acid in the cold, is converted into a compound, $C_{17}H_{13}ClO$, which crystallises from alcohol in flat needles with a silky lustre (m.p. 128°). When this compound is heated with alcoholic ammonia at 100°, it yields the condensation product, $C_{34}H_{24}O_2$ (m.p. 195° to 200°), already described.

When oxidised with dilute nitric acid, anhydracetonebenzil yields chiefly benzoic acid, together with paranitrobenzoic acid, oxalic acid, benzil, and a small quantity of a neutral nitrogenous substance crystallising in needles (m.p. 264°).

The authors have also commenced the study of the reactions of *anhydracetophenonebenzil*, $C_{22}H_{16}O_2$ (Japp and Miller, *Trans.*, 1885, 36), which was not supposed by its discoverers to contain a closed lateral chain. This compound appears to react both with 1 and with 2 mols. of phenylhydrazine, but neither of the derivatives thus formed could be obtained free from the other. When boiled with fuming iodhydric acid it is transformed like anhydracetonebenzil, parting with an atom of oxygen, and yielding a compound, $C_{22}H_{16}O$ (long flat prisms from alcohol, m.p. 92° to 93°). With alcoholic chlorhydric acid in the cold anhydracetophenonebenzil behaves like anhydracetonebenzil, forming a compound, $C_{22}H_{15}ClO$, which crystallises from alcohol in colourless slender needles, melting at 115°.

20. "*Condensation Compounds of Benzil with Ketones.*" By the same.

In order to ascertain whether the reaction in which anhydracetonebenzil and anhydracetophenonebenzil are formed (see foregoing note) is of general application, the authors have examined the action of benzil with various homologues of acetone. Caustic potash, of sp. gr. 1·27, was used as the dehydrating agent. In every case 1 mol. of benzil was found to react with 1 mol. of the ketone, eliminating 1 mol. of water. The intermediate additive compounds, the formation of which was observed in the case of the reactions of benzil with acetone and acetophenone (Japp and Miller, *Trans.*, 1885, 21 and 34), were not isolated.

The following compounds, which for purposes of nomenclature are *assumed* to be true homologues of anhydracetonebenzil have been prepared:—

*Methyl-anhydracetonebenzil*, $C_{18}H_{16}O_2$. From methylethylketone and benzil. Colourless thin prisms from alcohol; m.p. 179°.

*Dimethyl-anhydracetonebenzil*, $C_{19}H_{18}O_2$. From diethylketone and benzil. Colourless rhomboidal plates from alcohol; m.p. 150°.

*Ethyl-anhydracetonebenzil*, $C_{19}H_{18}O_2$. From methylpropylketone and benzil. Colourless minute needles from alcohol; m.p. 156°.

*Amyl-anhydracetonebenzil*, $C_{22}H_{24}O_2$. From methylhexylketone and benzil. Tufts of colourless slender silky needles from alcohol; m.p. 150·5°.

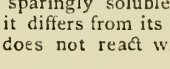
21. "*Constitution of Glycosine.*" By Francis R. Japp, F.R.S., and E. Cleminshaw, M.A.

Debus showed (*Phil. Trans.*, cxlviii., 209) that glyoxal reacts with ammonia according to the two equations—

I.. .. $3C_2H_2O_2 + 4NH_3 = N_4(C_2H_2)^{iv}{}_3 + 6H_2O.$
(Glyoxal. Glycosine.)

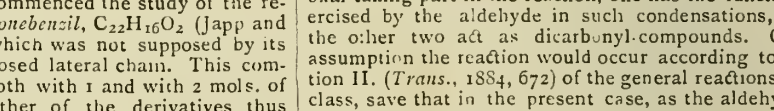
II.. .. $2C_2H_2O_2 + 2NH_3 = C_3H_4N_2 + CH_2O_2 + 2H_2O.$
(Glyoxal. Glyoxaline. Formic acid.)

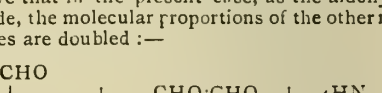
Radziszewski (*Ber.*, xv., 1495) has suggested that the second of these reactions occurs in two stages. In the first stage, 1 mol. of glyoxal is hydrolysed, yielding formic aldehyde and formic acid; in the second, the formic aldehyde reacts with another mol. of glyoxal and 2 mols. of ammonia, forming glyoxaline. Interpreting this second stage by the light of the condensations of dicarbonyl-compounds with aldehydes and ammonia, studied by one of the authors, glyoxaline would receive the formula—


(Japp, *Trans.*, 1883, 17).

This formula is in keeping with the reactions of the compound, and has found general acceptance.

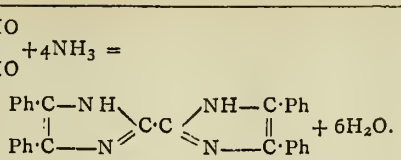
It occurred to the authors that the second of the above reaction in which glycosine is formed, might, in like manner, be interpreted as belonging to the class of dicarbonyl-aldehyde ammonia condensations, glyoxal being both a dicarbonyl compound and an aldehyde. It would only be necessary to assume that, of the 3 mols. of glyoxal taking part in the reaction, one has the function exercised by the aldehyde in such condensations, whilst the other two act as dicarbonyl-compounds. On this assumption the reaction would occur according to Equation II. (*Trans.*, 1884, 672) of the general reactions of this class, save that in the present case, as the aldehyde is a dialdehyde, the molecular proportions of the other reacting substances are doubled:—


(Glyoxal as dicarbonyl-compound. Glyoxal as aldehyde.)


Glycosine.

The glyoxal molecule of aldehyde function reappears as an oxalic acid residue in the formula of glycosine; the two glyoxal molecules of dicarbonyl function reappear in the form of two unsaturated groups—CH : CH—(comp. *Trans.*, 1884, 673). In this respect the reaction would belong to the numerous class involving mutual oxidation and reduction between similar molecules, to which class the aldehydes furnish the largest contingent.

If the foregoing view is correct, it should be possible to substitute, in the foregoing reaction, for the two glyoxal molecules of dicarbonyl function, two diketone molecules containing the group CO·CO. Thus, by the action of ammonia on a mixture of benzil and glyoxal, a *tetraphenyl-glycosine* should be formed:—



This was found to be the case. Tetraphenylglycosine, prepared by the above method, crystallises from alcohol in long, very slender, silky needles, $C_{30}H_{22}N_4,C_2H_6O$, which readily part with their alcohol of crystallisation. It melts above 300°. It forms unstable salts.

Debus formulates glycosine as a tertiary amine on the quadruple ammonia-type (see reaction I). The formula above suggested differs from this in containing two imido-groups. In order to prove the presence of two displaceable hydrogen-atoms, the authors heated glycosine with benzyl chloride, and obtained *dibenzylglycosine*,—

$$C_6H_4N_2(N{\cdot}C_7H_7)_2,$$

which crystallises from alcohol in oblique plates melting at 145°.

The authors have also prepared some new platini-chlorides of glycosine. In addition to the diacid salt, $C_6H_6N_4,H_2PtCl_6$, described by Debus, they have obtained a *monacid salt*, $(C_6H_6N_4)_2H_2PtCl_6$, the existence of which was suspected by Debus, and a *tetracid salt*,—

$$C_6H_6N_4(H_2PtCl_6)_2,$$

the latter being, of the three, that which is most readily prepared in a pure state.

A suggestion regarding the constitution of glycosine, similar to that here developed, has been thrown out by Wallach. He says, *Ber.*, xvi., 545, footnote):—"Glycosine probably stands in the same relation to glyoxaline as dioxalethyline to oxalethyline." It is to be remarked, however, that dioxalethyline appears to be derived from an isomeride of glycosine, in which the two glyoxaline complexes are united at a different point.

22. "*Diphenylglyoxaline and Methyldiphenylglyoxaline.*" By FRANCIS R. JAPP, F.R.S.

The author received from Mr. W. Palmer Wynne a small quantity of a base, melting at 218°, obtained, together with imabenzil, benzilimide, and benzilam by dissolving benzil in warm methylated spirit and saturating the solution with ammonia. This base remained in the last mother liquors.

The author failed to obtain it on substituting pure alcohol for methylated spirit. An attempt was then made to prepare it, employing methylated spirit; but the only basic substance obtained was methyldiphenylgloxaline (m. p. 235°), showing that the spirit contained aldehyde. An old specimen of wood-spirit was then used. A new base was then obtained, which was deposited from alcohol in crystals not unlike those of Mr. Wynne's base, but melting at 227°. This proved to be *diphenylglyoxaline*, formed by the condensation of formaldehyde, contained in the wood spirit, with benzil and ammonia. The crystals differ in form according as they are deposited from hot or from cold alcohol—the latter form only resembling that of Mr. Wynne's base.

Analysis of Mr. Wynne's base gave figures intermediate between those required for diphenylglyoxaline and methylglyoxaline. A mixture of these compounds in molecular proportions was therefore allowed to crystallise from alcohol. The solution deposited crystals indistinguishable from those of Mr. Wynne's base, and, like these, melting at 218°. Finally, Mr. L. Fletcher has established the identity by crystallographical measurements. The hydrochlorides of the mixed bases also crystallise together in forms identical with those of the hydrochloride of Mr. Wynne's base.

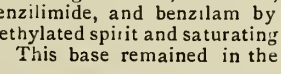
23. "*Dehydracetic Acid.*" By W. H. PERKIN, Jun., Ph.D.

It is known that if dehydracetic acid, $C_8H_8O_4$, be treated with alkalis, it is decomposed principally into acetic acid, carbonic anhydride, and acetone, a small quantity of malonic acid also being formed.

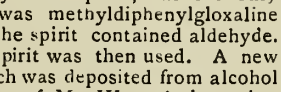
The author finds, however, that in the first place dehydracetic acid is converted into two molecules of acetoacetic acid, $C_8H_8O_4 + 2H_2O = 2CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH$. Dehydracetic acid reacts with phenylhydrazine and with hydroxylamine, forming the compounds—

$$C_7H_8O_3(N_2H{\cdot}C_6H_5)$$

and $C_7H_8O_3(N{\cdot}OH)$; and it therefore contains a carboxyl-group. The fourth oxygen-atom (not counting the carboxyl-group) is present neither as CO nor as OH, and the author therefore proposes the formula—



The action of aniline on methylic dehydracetate, in the author's opinion, is such as to prove the correctness of this expression, two substances, *methylic phenyldimethylpyridine carboxylate* and *phenyldimethylpyridone*, being formed, which are both pyridine-derivatives, viz.:—



An interesting synthetical proof of the correctness of the formula assigned to dehydracetic acid has lately been given by Conrad and Guthzeit (*Ber.*, xx., 154).

24. "*The Colouring-matter of Drosera Whittakeri.*" By Prof. E. H. RENNIE, M.A., D.Sc.

The author's attention was drawn to the presence of a red colouring-matter in the tubers of the above-mentioned *Drosera*, which grows plentifully on the hills near Adelaide, South Australia, by Prof. Tate. On inquiry he ascertained that Mr. Francis, of Adelaide, had extracted the colouring-matter by means of carbon bisulphide, and had found that it was volatile, and that beautiful tints could be produced with it on silk by means of various mordants, but had not continued the investigation. To separate the colouring-matter the tubers were heated with hot strong alcohol. After distilling off the spirit a little water was added, and the precipitated colouring-matter was then dried and sublimed; the product was a mixture of two substances differing in solubility in boiling alcohol and acetic acid. The less soluble was obtained in small brilliant red plates, canoe shaped under the microscope, which melted at 192° to 193°. Analysis gave numbers fairly agreeing with those required by the formula $C_{11}H_8O_5$, which may represent a *trihidroxy-methylnaphthaquinone*. The reactions of the substance, in so far as they could be studied with the small quantity of material at disposal, serve to support the view that it is thus constituted. The second substance was finally obtained in needles, quite different in appearance from the red plates, though to the eye of much the same colour. Under the microscope single crystals seemed yellow, but wherever they overlapped the colour appeared deep orange to red. It fused at 164° to 165°. Analysis gave numbers fairly agreeing with the formula $C_{11}H_8O_4$.

25. "*Further Notes on the Di-haloid Derivatives of Thiocarbamide.*" By GEORGE MCGOWAN, Ph.D.

The author has succeeded in obtaining dithiocarbamide dibromide in beautiful large rhombic crystals, by the action of bromine on an aqueous solution of thiocarbamide. At the ordinary temperature it is quite stable. By the further action of bromine on an aqueous solution this dibromide is converted into carbamide, or, more probably, in the first instance into cyanamide, hydrobromic and sulphuric acids being produced at the same time.

Sulphuretted hydrogen acts on dithiocarbamide dichloride, $(CSN_2H_4)_2Cl_2$, in alcoholic solution, producing thiocarbamide hydrochloride, $CSN_2H_4{\cdot}HCl$, and sulphur.

All attempts to prepare the dicyanide, $(CSN_2H_4CN)_2$, have failed. From the results of a number of experiments with different cyanides on thiocarbamide and its dichloride,

the author concludes that probably the dicyanide is formed, but immediately breaks up, the separated sulphur being taken up by the excess of cyanide present and thiocyanate formed.

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At the next meeting, on March 17th, there will be a ballot for the election of Fellows, and the following papers will be read:—

"The Action of Heat on Nitrogen Peroxide," by Dr. A. Richardson.

"The Formation of Naphthalene-sulphonic Acids by means of Sulphuric Anhydride," by Dr. Armstrong and W. P. Wynne, B.Sc.

## CORRESPONDENCE.

### MOLTEN IRON.

*To the Editor of the Chemical News.*

SIR,—I have not noticed the transparency of molten iron mentioned by Mr. Ramsay, but I have observed a rapid formation on the surface of molten iron of a curious reticulated geometrical pattern. The brilliant golden appearance of the fluid metal is very beautiful, and the operation of casting is a spectacle of deep interest.—I am, &c.,

C. R.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 5, January 31, 1887.

**Metals and Minerals from Ancient Chaldæa: on the Sources of Tin in the Ancient World.**—M. Berthelot.—The author has examined four tablets from the ruins of Nineveh; one is of gold, another of silver, a third of bronze (containing 10 per cent of tin), and the fourth of pure crystalline magnesium carbonate. A portion of a vase from Tello was found to consist of antimony, containing no appreciable trace of copper, lead, bismuth, or zinc. The author points out this extreme antiquity of the metallurgy of antimony as a remarkable fact. Tin is said to have been anciently obtained from the western parts of Afghanistan.

**Combinations of Sodium Glycerinate with the Monoatomic Alcohols.**—M. de Forcrand.—Not capable of useful abstraction.

**The Comparative Effects of Heat and of Solar Light.**—E. Duclaux.—All the actions of combustion which heat can produce may be also produced by light, but the converse does not hold good. There are many reactions which light alone seems able to set up. All these reactions may be summed up as a disturbance of the primitive molecule which is decomposed into simpler elements. These elements are few in number: they are, if we limit ourselves to volatile bodies, formic, acetic, and butyric acids, methylic and ethylic alcohols, and ethylic aldehyd. These stable groups are generally found the same with one and the same body, whatever the source from which it derives its oxygen. But this is not always the case. Thus lactic acid, if burnt by means of atmospheric oxygen, yields acetic acid, but produces butyric acid if it obtains its oxygen from the salts of mercury. These stable residues of combustion do not pre-exist as groups in the original molecule, but result from a new arrangement of the molecules during combustion. This is proved by the fact that they are found identical in bodies of different types, and are not always the same with one and the same body. These products contain a smaller number of molecules of hydrogen and carbon than the bodies whence they are derived. The sole exceptions to this rule, the formation of formic acid at the expense of oxalic acid, and that of butyric acid from lactic acid, disappear if we double the formulæ of oxalic and lactic acids. Potassium permanganate, which often acts in the cold and in darkness, does not yield other products than those resulting from the action of the sun and of heat. The bodies which it attacks best are those which are found least stable under other oxidising conditions. But if it does not occasion any novel facts, we may study with it very conveniently the circumstances of the experiment and the conditions of initial and final acidity or alkalinity which determine the result. These last conditions play a great part in the combustions made at the expense of oxygen, free or combined.

**The Properties of Inosite.**—M. Maquenne.—By the action of reducing agents inosite is converted into a phenol. By means of nitric acid it is transformed into tetra-oxy-quinone.

**A Compound of Paratoluidine and Cupric Chloride.**—E. Pomey.—On mixing hydrochloric solutions of these two substances and heating the liquid to a boil, golden-yellow crystals are gradually deposited.

**Composition of the Seeds of Holcus Sorgho, and their Application in Agricultural Industry.**—M. Bordas.—These seeds contain 42 per cent of starch, and, according to the author's experiments, yield, per 100 kilos., 26 litres of alcohol of a good quality.

No. 6, February 7, 1887.

**Red Fluorescence of Alumina.**—Lecoq de Boisbaudran.—The writer now finds that, after a very energetic ignition, alumina gives a red fluorescence in a vacuum under the action of the electric effluve, as had been pointed out by M. Becquerel. The latter savant added some remarks, which we reproduce elsewhere *in extenso*.

**Composition of the Ash of Cider.**—G. Lechartier.—The samples analysed gave quantities of ash varying from 1·7 to 4·9 grm. per litre. The proportion seems to augment at the same time as do the alcohol and the organic principles. From 80 to 92 per cent of the ash is soluble, consisting almost entirely of salts of potash. Soda is found only in traces, and lime not at all. The two predominant acids are the phosphoric and the carbonic. The insoluble portion of the ash contains lime, magnesia, silica, ferric oxide, and alumina.

**Electrolysis of Alkaline Solutions.**—M. Duter.—On electrolysing aqueous solutions of potassa, soda, baryta, or lime, the author has found the volume of oxygen evolved at the positive electrode strikingly less than the half of that of the hydrogen liberated at the negative electrode. There seem to be formed small quantities of a peroxidised compound, which is combined with the alkali in such a manner that it cannot be liberated by ebullition, but only by an acid. This compound may be a hydrogen peroxide, by the existence of which M. Berthelot explains various reactions, including that of potassium permanganate upon oxygenated water.

**The Principle of Maximum Work and the Laws of Chemical Equilibrium.**—H. le Chatelier.—The author concludes that:—"In phenomena of simple dissociation, the quotient of the absolute dissociation-temperature under the atmospheric pressure into the latent heat of decomposition at the same temperature, and referred to the volatilisation of a molecular weight of the gaseous bodies is a constant quantity. This law is applicable only to systems which are strictly comparable, that is, which

possess, at a given temperature, a determinate tension. This law may be approximated to the laws of Faraday and Gay-Lussac, which also establish relations between the chemical equivalents of bodies, and some of their physical properties.

**Action of Lead Oxide upon Certain Dissolved Chlorides.**—G. André.—The author has studied the behaviour of lead oxide with calcium, barium, strontium, and magnesium chlorides.

**Combinations of Potassium Glycerinate with Monoatomic Alcohols.**—M. de Forcrand.—A thermochemical memoir, which does not admit of useful abstraction.

**On Phospho-platinous Chloride.**—E. Pomey.—This compound, if brought in contact with water, exchanges the chlorine combined with the phosphorus for hydroxyl, yielding a tribasic acid.

**A Compound of Orthotoluidine and Copper Bichloride.**—E. Pomey.—This compound is not analogous in composition to the compound of cupric trichloride and paratoluidine, which the author has recently described. Both the copper and the chlorine are completely precipitable in their aqueous solution, the former by potassa and the latter by silver nitrate. This compound contains 5 mols. of orthotoluidine hydrochlorate to 1 of cupric chloride, whilst the para-compound contains only 2 mols.

**Di-isobutylamine Hydrochlorate and Chloroplatinate, and on Tri-isobutylamine Chloroplatinate.**—H. Malbot.—The di- and tri-isobutylamine chloroplatinates are respectively very distinct in figure, grouping, colour, lustre, crystalline system, cleavage, solubility, and deliquescence.

**On Gluconic Acid.**—L. Bourtroux.—The author points out that he obtained crystalline ammonium gluconate in 1880, and described it in the *Comptes Rendus* (xci., p. 236), and more in detail in the *Annales de l'Ecole Normale* (series 2, vol. x., p. 112). Herr Franz Volpert has, however, announced it as a novelty in the *Berichte der Deutsch. Chem. Gesell.* (October, 1886, p. 2621).

**Characters of Olive Oils.**—Albert Levallois.—The most constant characteristic of pure olive oil is its specific gravity, by which it may be distinguished from all the common oils except those of colza and of earth-nuts, which are easily distinguished by other characters. The action of bromine upon the fatty acids, when set at liberty, distinguishes olive oil very clearly from all the common oils except that of earth-nuts.

## MISCELLANEOUS.

**Action of certain Non-Metallic Elements upon Solutions of Silver and Copper Nitrates.**—J. B. Senderens.—The action of sulphur upon solutions of silver nitrate has been studied by the author and M. Filhol. It produces silver sulphide and free nitric and sulphuric acids. At 100° the reaction is complete only in very dilute solutions, and takes place very slowly. At common temperatures it requires some months for completion. With pulverised selenium the reaction is more rapid, the products being silver selenide and selenious acid. With tellurium the result is similar, but rather less rapid. Sulphur and selenium do not act upon solutions of copper nitrate, but tellurium reduces them partially with the aid of heat. Phosphorus and arsenic form with solutions of copper nitrate two compounds not yet described, a phosphide, $Cu_5P_2$, and an arsenide of a corresponding composition.—*Comptes Rendus.*

## MEETINGS FOR THE WEEK.

MONDAY, 14th.—London Institution, 5.
—— Medical, 8.30.
TUESDAY, 15th.—Institution of Civil Engineers, 8.
—— Royal Institution, 3. "Function of Respiration," by Prof. Arthur Gamgee, F.R.S.
—— Society of Arts, 8. "The Application of Gems to the Art of the Goldsmith," by Alfred Phillips.
WEDNESDAY, 16th.—Society of Arts, 8. "Machinery and Appliances Used on the Stage," by Percy Fitzgerald.
—— Meteorological, 7.
THURSDAY, 17th.—Royal, 4.30.
—— Royal Institution, 3. "The Science of Thought," by Prof. F. Max Müller, M.A., LL.D.
—— Chemical, 8. Ballot for the Election of Fellows. "On the Supersaturation of Salt Solutions," by W. W. Nicol.
—— London Institution, 6.
FRIDAY, 18th.—Royal Institution, 9. "Mental Differences between Men and Women" by G. J. Romanes, M.A., F.R.S.
SATURDAY, 19th.—Royal Institution, 3. "Sound," by the Right Hon. Lord Rayleigh.

## TO CORRESPONDENTS.

*Cassius.*—If possible do not let the paper occupy more than a page. The one just received is much longer than we like to insert.

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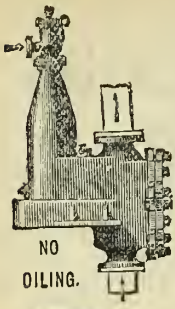


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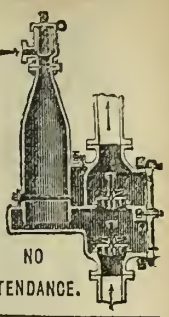

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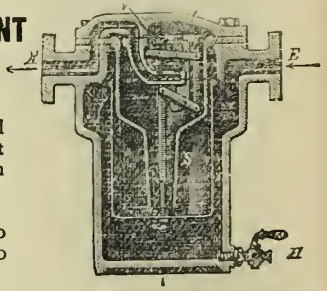


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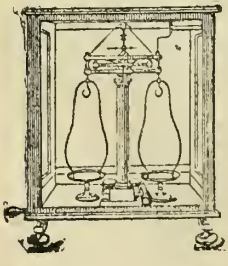

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THE CHEMICAL NEWS.

Vol. LV. No. 1425.

## ON RADIANT MATTER SPECTROSCOPY:—EXAMINATION OF THE RESIDUAL GLOW.*

By WILLIAM CROOKES, F.R.S. V.P.C.S.

(Continued from p. 110).

In the search for bodies giving discontinuous phosphorescent spectra I have submitted a great number of earths and combinations to the electric discharge in vacuo, and have noted the results. As the superficial phosphorescence apart from the composition of the emitted light has formed the subject of several recent papers by my friend M. Lecoq de Boisbaudran, before the *Académie des Sciences*, it may be useful if I place on record some of the more striking facts which have thus come under my notice. The bodies are arranged alphabetically, and, unless otherwise explained, were tested in the radiant matter tube in the form of ignited sulphates.

*Alumina*, in any of the forms which give the crimson line (λ6942—6937) has a very persistent residual glow. In the phosphoroscope rubies shine with great brilliancy. This phosphorescence of alumina has recently been the subject of a paper read before the Royal Society.†

*Antimony* oxide with 95 per cent of lime (in the form of ignited sulphate). White phosphorescence, the spectrum showing a broad space in the yellow, cutting the red and orange off. In the phosphoroscope the residual glow is very strong, and of a greenish colour. The spectrum of the residual light shows that the red and orange are entirely obliterated, leaving the green and blue very luminous. Antimony oxide with 99 per cent of lime gives a pale yellowish phosphorescence, which on heating turns red. In other respects it is like the 5 per cent mixture.

*Arsenious acid* with 99 per cent of lime gives a greenish white phosphorescence like pure calcium sulphate.

*Barium* 5 per cent, *calcium* 95 per cent.—The sulphates phosphoresce green, with specks of yellow and violet. The spectrum is continuous, with slight concentration in the red, great concentration in the green, and in the orange a broad black band hazy at the edges.

*Bismuth* 15 per cent, *calcium* 85 per cent, phosphoresces of a bright reddish orange. The spectrum shows a tolerably sharp and broad dark band in the red and orange, and a strong concentration of light in the green and blue; the spectrum being continuous and divided into two parts by a black band in the yellow, as in the case of the antimony-calcium spectrum. In the phosphoroscope the red and orange disappear and the green and blue remain. Bismuth 7 per cent, calcium 93 per cent.—The action is similar to the 15 per cent mixture, except the colour of the phosphorescence, which is whiter. In the phosphoroscope the red and orange below the dark band is cut off. With 2 per cent of bismuth the same phenomena occur. With 0·5 bismuth the phosphorescence is greenish blue and the spectrum is continuous, with strong concentrations in the orange and green. The phosphoroscope cuts off the red and orange.

*Cadmium* 1 per cent, *calcium* 99 per cent.—Similar to calcium sulphate, *q. v.*

*Calcium* sulphate was prepared from a colourless and transparent rhomb of Iceland spar which had been used for optical purposes. It was dissolved in nitric acid, the nitrate was decomposed with distilled sulphuric acid, and the ignited sulphate tested in the tube. The phosphorescence is bright greenish blue without bands or lines. In the phosphoroscope the colour is a rich green; the spectrum shows the red and orange entirely cut off, leaving the green and blue; the blue is especially strong.

Calcium sulphates prepared from Professor Breithaupt's calcites* were re-examined. All phosphoresce with the normal greenish blue glow of calcium, except No. 11, which gives a reddish glow. A minute trace of samarium was found in this calcite, but not enough to affect the colour of the glow. In the phosphoroscope all the specimens give a continuous spectrum beyond the yellow, the red and orange being cut off as usual.

*Chromium* 5 per cent, *calcium* 95 per cent, as sulphates, gives a pale reddish phosphorescence. In the phosphoroscope the colour is green and the red and orange are cut off. One per cent of chromium with calcium phosphoresces green in the cold, and becomes red when slightly heated. The behaviour of chromium with aluminium has already been described.†

*Copper* sulphate with 95 per cent calcium sulphate behaves like calcium sulphate.

*Diamonds* phosphoresce of various colours. Those glowing pale blue have the longest residual glow, next come those phosphorescing yellow: I am unable to detect any residual glow in diamonds phosphorescing of a reddish colour. A large diamond of a greenish hue, very phosphorescent, shines almost as brightly in the phosphoroscope as out of it.

*Glucina* phosphoresces of a rich blue colour. There appears to be no residual glow with this earth in the phosphoroscope.

*Lanthanum.*—All the specimens of lanthanum sulphate I have examined in the radiant-matter tube phosphoresce of a reddish colour, and give a broad hazy band in the orange, with a sharp line—$\frac{1}{\lambda^2}$ 280—superposed on it. This is identical with the line of Gε, one of the constituents of the samarium phosphorescent spectrum. Calcium added to lanthanum changes the colour of the phosphorescence from red to yellowish, and brings out yttrium and samarium lines, these metals being present as impurities; the Gδ and Gα lines are also seen, but the space which should be occupied by the Gβ green is now a dark space. I have shown that when Gδ, Gα, and Gβ are present in very small quantities with lime, the lines of Gδ and Gα are intensified, while that of Gβ is weakened. This new result seems to show that if only a small trace of Gβ is present with lime and lanthanum, the green line is not only suppressed, but the quenching action has actually extended so far as to neutralise that part of the continuous lime spectrum having the same refrangibility as the Gβ line, the result being a black space in the spectrum. In the phosphoroscope the line of Gε is visible at the slowest speed; Gδ comes in at an interval of 0·0035 second, and the Gα line immediately afterwards.

*Lead* sulphate, by itself, in the radiant-matter tube glows with a nearly white colour, giving a continuous spectrum. In the phosphoroscope the red and orange are cut off, leaving a strong concentration of light in the green and blue. Five per cent of lead added to calcium sulphate phosphoresces like lime.

*Magnesia* phosphoresces pink. Five per cent with lime, as sulphates, give a greenish phosphorescence, with a tendency to turn red as the powder heats. The Oriental ruby containing about between 1 and 2 per cent of magnesia, a mixture was prepared of acetate of alumina with 2 per cent of magnesia, and tested after ignition. It gave no spectrum or lines. This was done to see if the crimson line of aluminium might be due to the presence of magnesia.

*Nickel* added to calcium sulphate in the proportion of 5 per cent makes no alteration in the usual phosphorescent phenomena of calcium.

*Potassium* 5 per cent, added to calcium sulphate gives

* A Paper read before the Royal Society, Feb. 17, 1887.
† *Roy. Soc. Proc.*, 1887, vol. xlii., p. 25.

* *Phil. Trans.*, 1885, Part 2, p. 697.
† *Roy. Soc. Proc.*, 1887, vol. xlii., p. 28, *et seq.*

a bright phosphorescence and made the residual glow very persistent.

*Samarium.*—The phosphorescent behaviour of this body, alone and mixed with other substances, has been fully described in my paper on samarium.*

*Scandium*, either in the form of earth or sulphate, phosphoresces of a very faint blue colour, but the light is too feeble to enable a spectrum to be seen. Addition of lime does not bring out any lines.

*Sodium* sulphate mixed with an excess of calcium sulphate gives a greenish tinge to the usual colour of the phosphorescence. The sodium line is visible in the spectrum.

*Strontia* in the radiant-matter tube glows with a rich blue colour, showing in the spectroscope a continuous spectrum with a great concentration of light in the blue and violet. In the phosphoroscope the colour of the glow is bright green, showing in the spectroscope a continuous spectrum, with the red and blue ends cut off. A mixture of calcium sulphate with 5 per cent of strontium sulphate behaves like calcium sulphate alone.

*Thorium*, as oxide or sulphate, refuses to phosphoresce, and the tube rapidly becomes non-conducting. A tube with thoria at one end and a phosphorescent earth such as lime or yttria at the other end, and furnished with a pair of poles near each end, at a particular exhaustion is non-conducting at the thoria end, while it conducts at the yttria end. If the wires of the induction coil are attached to the poles at the thoria end, no current will pass; rather than pass through the tube, the spark prefers to strike across the spark gauge — a striking distance of 37 millimetres — showing an electromotive force of 34,040 volts. Without doing anything to affect the degree of exhaustion, on transferring the wires of the induction coil from the thoria to the yttria end, the spark passes at once. To balance the spark in air the wires of the gauge must be made to approach till they are only 7 millimetres apart, equivalent to an electromotive force of 6440 volts; the fact of whether thoria or yttria is under the poles making a difference of 27,600 volts in the conductivity of the tube. The explanation of this action of thoria is not yet quite clear. From the great difference in the phosphorescence of the two earths, it is evident that the passage of the electricity through these tubes is not so much dependent on the degree of exhaustion as upon the phosphorogenic property of the body opposite the poles. This view is supported by the fact that the thoria may be replaced by a metal wire, when the same obstructive action will result.

Lime does not give phosphorescent properties to thoria, if this earth be pure, but it brings out the lines of yttrium and samarium which are almost always present in small quantities in thoria unless it has been specially purified.

*Tin* with 95 per cent of lime gives the lime phosphorescence only.

*Thulium* and *erbium* together phosphoresce with a green light, giving the erbium spectrum already described before this Society.† There is, in addition, a faint blue line, apparently double (see "Ytterbium"). The addition of lime causes the mixture to phosphoresce of a pale blue colour. The spectrum now shows a bright blue band, in the same position as the faint double blue band seen in the absence of lime. The blue line of G$\alpha$ is also seen, and a faint line of G$\delta$. The deep red line of G$\eta$, one of the constituents of the ordinary yttria spectrum, is prominent in this spectrum.

*Tungsten* and *uranium*, each mixed with 95 per cent of lime, only give the lime spectrum.

*Ytterbium.*—I have not yet succeeded in preparing this body of trustworthy purity; but through the kindness of Prof. Clève, M. de Marignac, and Prof. Nillson I have been enabled to experiment with specimens of ytterbia prepared by these chemists. Prof. Clève's ytterbia, in the form of sulphate, gives in the radiant-matter tube a blue phosphorescence, the spectrum of which shows a strong double blue band,* together with traces of the G$\delta$ and the erbia green lines. The addition of lime broadens the blue band and makes it single. Prof. Clève writes that this ytterbia may contain some traces of thulia, perhaps also of erbia, but scarcely any other impurities. Measurements in the spectroscope give the following approximate results.

| Scale of Spectroscope. | $\lambda$ | $\frac{1}{\lambda^2}$ | Remarks. |
|---|---|---|---|
| 8·63 | 4626 | 4673 | Commencement of first blue line. This edge is very hazy. |
| 8·54 | 4574 | 4780 | Centre of the first blue line. |
| 8·45 | 4524 | 4885 | End of first blue line. |
| 8 44 | 4518 | 4898 | Centre of dark interval between the two blue lines. |
| 8·40 | 4475 | 4994 | Centre of second blue line. This line is narrower than the first line. |

The following are measurements taken with the mixture of this ytterbia and lime:—

| | | | |
|---|---|---|---|
| 8·71 | 4674 | 4577 | Up to this point there is the continuous spectrum of lime. Here a black space commences. |
| 8·515 | 4555 | 4819 | Commencement of a hazy blue band. |
| 8·475 | 4538 | 4855 | End of hazy blue band. This band is of considerable brilliancy. |

These blue bands are seen much fainter without lime, and are about as strong in the mixture of thulia and erbia with lime described above. I had ascribed them to ytterbia, when Professor Nillson kindly forwarded me a small specimen of ytterbia, considered by him perfectly pure, and used for his atomic weight determinations. This ytterbia gives absolutely no blue bands. The origin of these bands therefore remains uncertain

Ytterbia from Professor Nillson, in the form of sulphate, refuses to phosphoresce without the addition of lime. When lime is added it only brings out traces of the phosphorescent bands of G$\varepsilon$, G$\beta$, and G$\alpha$. Evidently these are impurities.

Ytterbia from M. de Marignac is identical with that from M. Clève, as far as my examination can go. In sending me this ytterbia M. de Marignac warned me that he was very far from thinking it pure.

*Yttrium.*—During the fractionation of the higher fractions of yttria (+6, 118 and 119), a very sharp green line sometimes makes its appearance, situated between G$\beta$ and G$\gamma$ (approximate position on the $\frac{1}{\lambda^2}$ scale, 325). It is very faint, and is not connected with the orange line of S$\delta$, although it is as sharp. The yttria showing these lines phosphoresces of a transparent golden yellow colour, the fractions at the other end phosphorescing yellowish green.

I have previously described the action of a large number of bodies on the phosphorescence of samarium.† The experiments resulting in the following observations were tried at about the same time. I will describe them in alphabetical order. Unless otherwise mentioned all the mixtures were in the form of anhydrous sulphates.

*Yttrium* 5 per cent, *aluminium* 95 per cent, gives a good yttria spectrum; the blue line of G$\alpha$ is very distinct, and the double green of G$\beta$ is well divided. In the phosphoroscope the G$\beta$ and G$\alpha$ lines first appear simultaneously, then the G$\delta$ line.

* *Phil. Trans.*, 1885, Part 2, pp. 709—721.
† *Roy. Soc. Proc.* vol. xl., p. 77, fig. 1, Jan. 7, 1886.

* This is the band spoken of in my Royal Society paper of June 9th last (*Roy Soc. Proc.*, 1886, vol xl., p. 507), provisionally called S$\gamma$ and ascribed to ytterbia. If it is not due to ytterbia it is a new body
† "On Radiant Matter Spectroscopy. Part 2—Samarium." *Phil Trans.*, 1885, Part 2, pp. 710—722.

*Yttrium* 99·5 per cent, *bismuth* 0·5 per cent.—The spectrum is bright, and on close examination a trace of samarium green, Gγ, is to be detected forming a wing to the Gδ line. In the phosphoroscope the citron line of Gδ entirely disappears and the samarium double green line, which out of the phosphoroscope is almost obscured by the great brightness of Gδ, now appears distinctly, together with the green Gβ line. Yttrium 95 per cent, bismuth 5 per cent, gives the usual yttria spectrum. No Gδ line appears in the phosphoroscope at any speed. At first only the Gβ line is seen, and next the Gα line appears, as in yttria. On gradually increasing the percentage of bismuth the spectrum of yttria grows fainter, until with 95 per cent of bismuth the phosphorescence is bad and the spectrum faint.

*Yttrium* 5 per cent, *cadmium* 95 per cent, gives a brilliant phosphorescence, but the spectrum is almost continuous. In the phosphoroscope a faint concentration of light is seen in the green, which becomes sharper as the speed increases.

The action of calcium on the phosphorescence of yttrium has already been described.

*Yttrium* and *Cerium*.—Cerium has the effect of deadening the brilliancy of the yttrium spectrum in proportion to the quantity added. All the bands remain of their normal sharpness.

*Yttrium* 5 per cent, *copper* 95 per cent, phosphoresces very feebly.

*Yttrium* 90 per cent, *didymium* 10 per cent.—This mixture gives a good yttria spectrum. Yttrium 70 per cent, didymium 30 per cent, phosphoresces very fairly and gives all the usual lines.

*Yttrium* 50 per cent, *didymium* 50 per cent, refuses to phosphoresce. The tube is either too full of gas to allow the phosphorescence to be seen or it becomes non-conducting. When the mixture is illuminated by the glowing gas the absorption lines of didymium in the green are seen. With higher proportions of didymium the same results are produced. On adding 25 per cent of lime to the mixture containing 50 per cent of didymium the yttria spectrum is brought out very well. Lime added to a mixture of 10 per cent yttria and 90 per cent didymium brings out the yttrium spectrum fairly, but the tube soon becomes non-conducting.

*Yttrium* 5 per cent and *glucinum* 95 per cent gives a bright phosphorescence, but the definition of the spectrum lines of yttria is bad.

*Yttrium* 5 per cent, *thallium* 95 per cent.—No spectrum is given by this mixture, it turns black and refuses to phosphoresce.

*Yttrium* 5 per cent, *tin* 95 per cent, phosphoresces faintly, the lines being very indistinct.

*Yttrium* 5 per cent, *titanium* 95 per cent, acts like thoria, and the tube becomes non-conducting.

*Yttrium* 5 per cent, *tungsten* 95 per cent.— This phosphoresces of a bright yellow colour, the spectrum is brilliant, but the lines are not sharply defined. In the phosphoroscope the colour becomes greenish, and the spectrum shows only the green lines of Gβ.

*Yttrium* 5 per cent, *zinc* 95 per cent. — The phosphorescence is of a pale yellowish white, and the spectrum is very brilliant, being equal to that shown by 30 per cent of yttrium with barium, calcium, magnesium, or strontium. In the phosphoroscope the colour becomes reddish and the Gβ green line is the first to come. No citron line is seen. If the yttrium contains a trace of samarium, the samarium spectrum, which is scarcely seen under ordinary circumstances, now comes out distinctly.

*Zinc* sulphate mixed with 95 per cent of calcium sulphate phosphoresces a bright bluish-green colour; the spectrum contains no bands or lines.

*Zinc sulphide* (Sidot's hexagonal blende*).—This is the most brilliantly phosphorescent body I have yet met with. In the vacuum tube it begins to phosphoresce at an exhaustion of several inches below a vacuum. At first only a green glow can be seen; as the exhaustion gets better a little blue phosphorescence comes round the edges. At a high exhaustion, on passing the current the green and blue glows are about equal in brightness, but the blue glow vanishes immediateiy the current stops, while the green glow lasts for an hour or more. In the phosphoroscope the blue glow is only seen at a very high speed, but the green glow is seen at the slowest speed, and the body is almost as bright in the instrument as out of it. Some parts of a crystalline mass of blende which, under the action of radiant matter, leave a glow with a bright blue colour, leave a green residual light when the current ceases; other parts which glow blue become instantly dark on stopping the current.

(To be continued).

* *Comptes Rendus*, lxii., 1866 pp. 999—1001 lxiii. 1866 pp. 188—189.

## THE DETERMINATION OF THE TOTAL ORGANIC CARBON AND NITROGEN IN WATERS BY MEANS OF STANDARD SOLUTIONS.*

By CHARLES A. BURGHARDT, Ph.D.

THE Members of this Society may remember that I read before them a preliminary note on a method for rapidly determining the total organic carbon in waters, on the 23rd of February, of this year. The communication I make to-day must also be considered as a "preliminary note," because the method of analysis applied in this case is entirely distinct from that given in my first communication, and I wish to collect all the material I can before venturing to criticise fully the work of other chemists in regard to the analysis of waters.

I have during the last six months had many excellent opportunities for thoroughly testing the working of the chromic acid method for the determination of organic carbon in waters of various qualities, and am perfectly certain that the results are eminently satisfactory so far as the *complete* estimation of the organic carbon is concerned. I wished, however, to estimate in an easy and accurate manner the total amount of organic nitrogen, and also to make the determination of the organic carbon simpler and less complicated. There is no doubt at all in my mind, in the case of a sewage-polluted stream or well, that the determination of the carbonic acid gas given off (after driving off the free dissolved carbonic acid gas at 94° C.) on heating the water to 100° C. is a most valuable portion of water examination, because *that particular carbonic acid gas* has been formed entirely *from organic matters in a partially decomposed or putrescent condition.* This organic matter is entirely lost in the course of evaporation as required by the "combustion process," and it certainly constitutes a large proportion of the total organic matter present in a sewage-polluted water,—a fact which has been proved by my analyses of the Irwell water, and experiments made with it. I find that Prof. J. W. Mallet, F.R.S., of the University of Virginia, mentions (in his Report to the National Board of Health, Washington, 1880) the source of error: he says—"As regards the combustion process we find distinct confirmation of the existence of the two forms of constant error which have been pointed out as affecting the Corporation. The weaker the solution—or, in other words, the larger the quantity of water to be evaporated for a given amount of organic matter—the less is the amount of organic carbon contained, indicating relatively greater loss of this element. On the contrary, the weaker the solution, or the greater the quantity of water to be evaporated, the larger is the figure for organic nitrogen,

* A Paper read before the Manchester Literary and Philosophica Society, December 14th 1886.

indicating relatively greater gain of this element from the atmosphere."

I conclude, therefore, that in many cases it will be necessary to determine the carbon *corresponding to the organic matter volatile* at 100° C. in the manner I point out in my previous paper on the subject.

As one proof out of many which I could lay before you I will give an analysis made by the "ammonia process," the "permanganate process," and the "chromic acid process," the sample being one taken from the Irwell at Throstlenest, on the 19th of February, 1886, and the results are expressed in grains per gallon:—

(1) Free ammonia .. .. 0·196.
Albumenoid ammonia . 0·226.

(2) Oxygen required to oxidise the organic matter:—

| In three minutes. | One hour. | Three hours. |
|---|---|---|
| 0·413 | 1·442 | 1·694. |

(3) Carbonic acid given off on heating to 96° C. = 1·512.
,, ,, ,, 100° C. = 7·224.
Carbonic acid estimated separately by precipitation with ammoniacal barium chloride solution (therefore as carbonates) .. = 2·681.
Carbonic acid obtained by oxidation by means of chromic acid .. .. .. .. = 2·733.

As the water was carefully heated to a temperature not exceeding 96° C., until all the *dissolved free* carbonic acid was liberated and no more was given off, it is clear from these results that the carbon of the 7·224 grains of carbonic acid gas given off on boiling the water (1·9701 grains) was derived from organic matter undergoing rapid decomposition at 100° C., *and from no other source.*

I venture to think that a result of this kind shows the necessity of devising a method for the accurate determination of the carbon in the water itself, and not by burning the residue obtained on its evaporation, and then measuring the amount of carbonic acid gas thus obtained.

On comparing the total carbon obtained by my process (calculated from the two amounts of carbonic acid gas, viz., 7·224+2·733=9·057 $CO_2$=2·667 carbon), with the amount of carbon corresponding to the amount of oxygen required to oxidise it in three hours, viz., 2·329 grains of carbon, it is evident that there is a loss of 14·51 per cent of the carbon in the permanganate process, or, in other words, *that* process in this particular instance failed to estimate the amount of carbon present by 14·51 per cent. I have found, however, in some cases that it expresses fairly well the amount of organic carbon present in a water, but it cannot be safely relied upon to do so.

I will pass from this part of the subject to the modification of my process which I have arrived at after considerable experiment and expenditure of time.

The principle of my first process consisted in the oxidation of the carbon in the water to carbon dioxide, this being effected at the expense of the chromic acid, consequently the latter must be reduced to a lower oxide of chromium during the process. Bearing this fact in mind I at last concluded that a determination of the amount of oxygen given off by the chromic acid to the carbon must necessarily give me the equivalent to it of carbon in the water. The reaction which occurs on adding a solution of chromic acid in water (acidulates with sulphuric acid) to water containing organic matter is as follows, viz.:—

$$4CrO_3+6SO_4H_2+3C=3CO_2+2Cr_2(SO_4)_3+6H_2O.$$

As an excess of chromic acid is always used in the process, all that is therefore necessary is to estimate the amount of chromic acid still remaining unreduced, by means of some convenient standard solution, which is itself oxidised by the excess of chromic acid. In order to carry out the process I first prepare the necessary standard solutions.

*Preparation of the Standard Solutions.*

1st. Ordinary decinormal permanganate of potassium solution (3·16 grms. to 1 litre).

2nd. A solution of pure chromic acid in pure distilled water (about 10 grms. to the litre).

3rd. A solution of ferrous sulphate in pure distilled water (about 25 grms. to the litre).

First I titrate the ferrous sulphate solution by means of the decinormal permanganate solution, and find in this way how much permanganate is equal to the ferrous sulphate solution, and, knowing the "oxygen value" of the permaganate solution, it at once furnishes me with the "oxygen value" of the ferrous sulphate solution.

Next I take a known volume of the chromic acid solution and titrate it with the standard ferrous sulphate solution, until all the chromic acid is reduced, a point easily seen with a little practice, as the slightly yellowish green colour at the final stage of the titration changes sharply to a bluish green on the addition of *one* drop, and one further; at this point using a solution of ferricyanide of potassium as an indicator, it is seen that there is a very slight indication of excess of ferrous sulphate present, whereas, before the addition of this drop, there was no such indication. This operation furnishes the value of the chromic acid solution *expressed as ferrous sulphate solution.*

The chromic acid solution will keep a very long time, but it is advisable to prepare the ferrous sulphate solution freshly at least once a week.

Having prepared the standard solutions the process of analysis is as follows, viz.:—

*Determination of the Organic Carbon.*

Place 250 c.c. of the water sample in the "boiling flask," of 16 oz. capacity, add 100 c.c. of the chromic acid solution, and 10 c.c. of strong sulphuric acid, and boil for about thirty minutes, when the oxidation of the organic matter is complete, the water in the "boiling-flask" having become perfectly clear. I then dilute the contents of the flask to 1 litre, and take out 100 c.c. of this solution and titrate it with the standard ferrous sulphate solution until there is a very slight excess of the latter. By calculation I find how much *carbon* the *oxygen* thus indicated is equal to.

*Determination of the Organic Nitrogen.*

Contrary to expectation I found that the nitrogen in organic compounds is converted into ammonia and not into nitric acid or nitrous acid by the action of chromic acid or sulphuric acid. A similar fact was discovered by Kjeldahl (*Zeits. Anal. Chem.*, xxii., 366), where he describes the conversion into ammonia of nitrogenous matter, by boiling it with strong sulphuric acid, phosphorus pentoxide, and powdered manganate of potassium.

Märker tested this method thoroughly (*Zeits. Anal. Chem.*, xxiii., 553—557) against the well-known method of Varrentrapp and Will, and found the results by Kjeldahl's method sufficiently correct.

To determine the organic nitrogen in the water I take 250 c.c. or more of the solution obtained by the previous organic carbon process (the solution made up to 1 litre), place it in the "boiling flask," pour down the funnel tube a perfectly ammonia-free caustic soda solution *in excess*, and attach the exit-tube of the "boiling-flask," to the Liebig's condenser and flask as used in the organic carbon determination, placing, however, in this case, about 50 c.c. of ammonia-free water and a few drops of pure hydrochloric acid into the "receiving-flask." It is also better to take the necessary precautions to prevent the sucking of the water in the "receiving flask," back into the "boiling flask." I boil the contents of the flask for about thirty minutes (keeping the condenser cool), then I make up the condensed water in the "receiving-flask" to one litre, take out 100 c.c., and determine the amount of ammonia present in it in the usual way with Nessler's reagent, and calculate how much nitrogen it corresponds to.

I do not lose any nitrogen by this method, because all the ammonia evolved from the "boiling-flask" is passed

into cold acidulated water, whereas by the old "ammonia-method," the violent bumping in the retort often drives steam, and no doubt ammonia, right through the long condensers used in that process, consequently there must be a loss of ammonia.

I have not yet had sufficient time to work out by my method the limits at which a water can be said to be *unsafe* to drink, but I hope to do so shortly.

*Example of Analysis of Sewage Water from Devizes.*

(1) *Ammonia Process.*

Contains free ammonia .. .. 0·560 grains per gallon.
" albumenoid ammonia :—
1st distillate.. .. 1·435 "
2nd distillate .. 0·420 "
Total ammonia .. 2·415
= nitrogen 1·988 grains per gallon.

The albumenoid ammonia in the first distillate was obtained by distilling in the usual way until no more ammonia could be estimated by Nessler's reagent. The retort and apparatus was then carefully closed for the night, and the contents distilled again next morning, the result being a second crop of ammonia (distillate No. 2).

(2) *Oxygen Process.*

Oxygen required to oxidise organic matter, in grains per gallon.

| In three minutes. | One hour. | Three hours. |
|---|---|---|
| 1·862 | 3·472 | 5·48. |

5·48 grains of O = 4·11 grains of C.

(3) *Chromic Acid Process.*

(*a*) by titration with ferrous sulphate.

250 c.c. of sample taken, added 20 c.c. of the chromic acid solution, and 10 c.c. of strong sulphuric acid, and boiled for thirty minutes, diluted to 1 litre, and took 100 c.c. of this solution with the standard ferrous sulphate solution; required 19·0 c.c. of $FeSO_4$, therefore the whole litre would require 190 c.c. $FeSO_4$.

20 c.c. of the chromic acid solution required, on being titrated, 210·0 c.c. of the ferrous sulphate solution.

210 − 190 = 20 c.c. of $FeSO_4$ (equal to the chromic acid reduced by the carbon in the water).

*Strength of the* $FeSO_4$ *Solution.*

3·6 c.c. $FeSO_4$ = 100 c.c. of permanganate solution (5 c.c. permanganate solution = 0·0004 oxygen).

3·6 c.c. $FeSO_4 = 0{\cdot}0004 \times 20 = 0{\cdot}008$ oxygen.

20 c.c. " $= \frac{0{\cdot}0008 \times 20}{3{\cdot}60} = 0{\cdot}004444$ &c. oxygen.

or 9·3824 grains of carbon per gallon.

(*b*) By the lime-water method and distillation.

50 c.c. lime-water = 50 c.c. standard oxalic acid.
1 c.c. oxalic acid solution = 0·001 $CO_2$.

250 c.c. of the Devizes sewage-water taken.

Took 200 c.c. lime-water altogether and titrated back with 72 c.c. oxalic acid solution.

128 c.c. of lime-water used.
128 c.c. = 0·128 $CO_2$.
= 9·72 grains of carbon per gallon.

This contained a little carbon present as carbonate.

*Sale, Cheshire, Sample of Sewage Water.*

*Chromic Acid Process.*

By lime-water method .. 0·1444 grain C.
By $FeSO_4$.. .. .. .. 0·1487 "

**University of London.**—We are requested to call attention to the change which it has been necessary to make in the time of holding the ensuing Matriculation Examination (viz, from the week commencing Monday, June 20th, to the preceding week, commencing Monday, June 13th).

ON THE

## PHOSPHORESCENCE OF CALCIUM SULPHIDE.

By M. EDMOND BECQUEREL.

In the last number of the *Comptes Rendus* is a paper by M. Verneuil entitled "The Determining Causes of the Phosphorescence of Calcium Sulphide," containing the results of very interesting experiments, which in M. Verneuil's opinion confirm the views put forward by the author on the influence of foreign matters in modifying the molecular condition of phosphorescent calcium sulphide. He believes that it is interesting to recapitulate some of the inducements which have led him to think that the modifications undergone by this compound may depend on a change of physical condition.

Calcium sulphide, in fact, like most of the calcium compounds, is phosphorescent, but it presents differences according to its preparation, according to the duration, the intensity, and the refrangibility of the luminous rays emitted. Even when no notable effect is manifested on exposing it to light and placing it afterwards in a dark chamber, it gives a luminous emission in the phosphoroscope. Pure calcium sulphide, which M. Verneuil has prepared, and of which he has kindly forwarded two specimens to the author, behaves in this respect like the sulphides which the latter had prepared previously; it is faintly luminous in the phosphoroscope when it receives the action of the solar rays.

But the duration of the phosphorescence of this substance may be much increased by the presence of foreign matters added to the mass on its preparation, even though they may be very slightly or not at all phosphorescent; at the same time the luminous intensity is heightened, and the colour of the rays emitted is modified. This follows from observations which the author has made long ago, and which he is still pursuing. According to these calcium phosphide prepared from the lime of Iceland spar, arragonite, or other sources,—or with calcium carbonate, with which different bodies were mixed, especially metallic sulphides, potassium or sodium salts (potassium persulphide, sodium chloride, thiosulphate, &c.),—yields artificial phosphori, very persistent, more or less brilliant and luminous with different colours. He mentions the effects produced by traces of potassium persulphide and manganese peroxide. The former yields a very luminous matter with green phosphorescence; with manganese peroxide the phosphorescence is orange-yellow. The addition of lithium carbonate to the lime in the preparation of the sulphide yields, according to Dr. Strohl's observation, a substance having a very brilliant green phosphorescence of a peculiar shade. It must be observed that potassium, manganese, and lithium sulphides are scarcely luminous, or not at all.

The temporary modifications which certain phosphorescent preparations may undergo by the action of heat likewise support the hypothesis which ascribes the different shades given by different preparations of a phosphorescent sulphide to the varied physical states of such sulphide. Thus one of the calcium sulphides—which at ordinary temperatures, and prepared under the conditions which the author has formerly indicated ("La Lumière," vol. i., p. 389), gives out a green light—has a blue phosphorescence at 100° and a brilliant violet-blue between 200° and 300°. But at ordinary temperatures it recovers its green phosphorescence. It thus becomes temporarily capable of emitting, when heated, and after the previous action of luminous radiation, rays of the same refrangibility as those emitted permanently at common temperatures by a sulphide prepared in another manner.

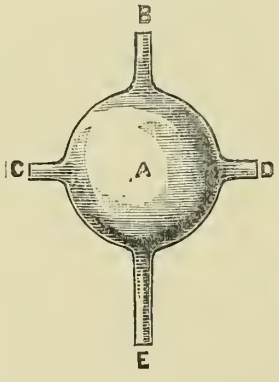
From the temporary influence of a temperature, not very elevated, not capable of decomposing the sulphide, and producing merely a change in the physical condition of the body, we may infer that effects of the same order may be produced permanently in the preparation of calcium sulphide by other processes.

Another phosphorescent substance, strontium sulphide, prepared with caustic strontia and sulphur, presents changes still greater, since after exposure to light it emits a violet-blue phosphorescence at $-20°$; at $+40°$ it becomes light blue, at 90° greenish yellow, and at 150° orange, resuming at each temperature the corresponding luminous power. Thus this sulphide, taken at different temperatures, reproduces after insolation temporarily and successively almost all the prismatic colours, and consequently all the effects obtained permanently at common temperatures with different preparations of strontium sulphide.—*Comptes Rendus* (civ., p. 551).

## METHOD OF PREPARING GRAPHITOIDAL CARBON FOR ELECTRICAL INCANDESCENCE.

By H. N. WARREN, Research Analyst, &c.

Having recently had occasion to pass a series of electrical sparks over certain substances in a current of hydrogen gas, for the sake of simplifying the arrangement I substituted for the hydrogen coal-gas, and on observing after the lapse of a short time a somewhat small but dense black point projecting from the negative wire. I at once stopped the experiment with a view of ascertaining the cause of the above phenomenon, and finding it to consist entirely of graphitoidal carbon. I made use of the following apparatus, consisting of a glass globe, A, con-




taining four openings or necks. The coal-gas being admitted at the tube E, and consumed at B; at C and D are two platinum wires, the one at D being somewhat the longer, so as to allow of its gradual withdrawal through the cork inserted in the neck D. The extremities of both wires were connected respectively with an induction coil capable of giving an intense half-inch spark. After an interval of a few minutes a blackish point was observed projecting from the negative wire, and nearly touching the positive. On withdrawing the latter a slight distance from the negative, the graphite stem (so to call it) lengthened itself as before towards the positive pole, and in so doing doubled its original length; and on repeating the former operation of partially withdrawing the positive wire, a continuous line of graphitoidal carbon was obtained measuring from an inch to an inch and a half.

On being withdrawn from the apparatus it was found to consist, although fine as regards diameter, of very hard graphitoidal carbon, and exhibited when under the microscope a decided crystalline structure.

On being connected as before with the induction coil and suspended in an atmosphere of oxygen, on connection with the battery being made it was dissipated with great brilliancy, leaving no residue. A similar piece gave a most intense and durable light in vacuum.

I have lately varied the experiment by introducing for electrolysis a mixture of coal-gas and silicon fluoride, as also boron fluoride, with the object of forming a still denser and more durable carbon in admixture with silicon or boron, but have hitherto only partially succeeded.

## APPARATUS FOR THE EXAMINATION OF WATER BY DR. KOCH'S PROCESS.

By CHAS. W. FOLKARD.

The necessity for special apparatus is always a drawback, and, in common with many others, the author has endeavoured to use the ordinary laboratory appliances alone in carrying on bacteriological examinations of water.

Test-tubes, about 7 inches long and ¾ inch in diameter, are used to receive the nutrient jelly. They are closed by a plug of cotton-wool, which is tied by thread round a piece of glass tube bent at right angles and drawn off at one end. The bent tube has a capacity of 1 c.c., and

serves for the introduction of the measured quantity of water for experiment. The whole is sterilised in the usual way.

The water, of which a sample is required to be examined, is allowed to run through a piece of ¾ inch india-rubber tube (pierced with a small hole in the middle, and furnished with a glass jet at the end) till all germs on the tube have been washed away.

The capillary end, *a*, is passed through the hole in the india-rubber tube, and sufficient time allowed for any germs on it to be washed off. The capillary end is then broken off by the fingers, or by a pair of pliers, while it is inside the india-rubber tube.

The water (which is of course running all the time) fills the bent tube, being assisted if necessary by partially stopping the glass jet for an instant. The bent tube is then withdrawn, the capillary end sealed in the flame, and the 1 c.c. of water transferred to the test-tube by shaking.

By allowing the gelatin to set when the test-tube is in a horizontal position, the "centres" can be easily counted

and examined, being spread over an area of 4 or 5 square inches.

The above is merely a simplified form of the well-known Aitken's test-tube, enabling the operator to dispense with all but the ordinary laboratory apparatus. The transfer of the solution from the test-tube to a glass plate, with the attendant risk of aërial contamination, is also avoided.

The desirability of taking the tube to the water supply, instead of bringing a sample of water to the laboratory, is obvious, and in the majority of cases there is no great difficulty in doing so.

Chiswick, March 8, 1887.

## ON NEW ZEALAND GRAPHITE.

By R. W. EMERSON McIVOR, F.I.C., F.C.S.

Large quantities of graphite exist at Pakawan Bay, in Golden Bay, N.Z., which will sooner or later be turned to commercial account. When in Nelson a year or two ago I was called upon by Mr. J. Gilmour, one of the lessees of the ground, to examine the material "as dug out of the ground." The following are my analyses of dried samples:—

| | No. I. | No. II. |
|---|---|---|
| Carbon.. .. .. | 34·99 | 51·45 |
| Ash .. .. .. | 65·01 | 48·55 |
| | 100·00 | 100·00 |

No. II. appears to be as good in quality as much of the graphite sold for common purposes in this country.

## RIDSDALE'S ROTARY CHROMOMETER.

Mr. C. H. Ridsdale, a short time since, in a paper to the Society of Chemical Industry,* in giving his experience on the estimation of very low percentages of carbon, stated that at the North-Eastern Steel Works at Middlesborough, where they constantly tested steels containing only from 0·02 to 0·05 per cent of this body, they had adopted Stead's alkali method as being rapid and very accurate, and he also described an apparatus for comparing the depths of tint of the very weak solutions obtained in this method.

In Stead's alkali method the steel is dissolved in nitric acid, and caustic soda added, which precipitates ferric hydrate and causes the combined carbon to pass into solution, and the liquid is then made up to a definite bulk, filtered, and the filtrate compared in the apparatus with a standard treated in the same way. The relative height of the column of liquid required to give equal depth of tint indicates the carbon content.

The apparatus is the outcome of long practical experience with this class of work, and is specially designed to avoid fracture, and for rapid and reliable work. It consists essentially of three comparison tubes, into one of which the solution to be tested is put; and in the other two, columns of standards of different strength can be raised or lowered by means of glass syringes. The apparatus can be revolved to overcome the influence of side light, and to obtain better comparison.

As the standards are pumped in and out of their reservoirs without taking to pieces at all, there is no liability to breakage as in previous chromometers.

The Æolus Waterspray Company have removed from No. 235 to No. 124, High Holborn, London, W.C.

* Read at Newcastle; published in the *Journal o the Society of Chemical Industry*, No. 11, vol. v.

# PROCEEDINGS OF SOCIETIES.

## MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

*Ordinary Meeting, January 25th, 1887.*

Prof. W. C. Williamson, LL.D., F.R.S., Vice-President, in the chair.

The following communication from the Secretary of the Manchester Jubilee Exhibition, addressed to the Honorary Secretaries of the Society, was read:—

The Photographic sub-section of the Jubilee Exhibition are devoting a portion of their space to a history of the rise and progress of the Photographic Art, and are anxious to hear of specimens or apparatus bearing upon this department of the subject. They will be obliged by possessors of any such objects of interest communicating with them at the offices, Albert Chambers, Albert Square, Manchester.

Professor W. C. Williamson, LL.D., F.R.S., brought before the Society the substance of a communication which he had received from James Nasmyth, Esq., of Penshurst. Experimenting upon the action upon glass of the coke used for heating the boilers of locomotives, Mr. Nasmyth found that a piece of hard coke "possesses the diamond property of cutting a clean diamond-like cut into glass, not a mere scratch, but a true cut through it." Mr. Nasmyth further points out that if this is done when the glass is held at a slight inclination to the direction of the sun-light showing through it, the cut thus made gleams with prismatic rays. These effects all correspond so closely with those produced when a diamond is similarly used, as to suggest that the coke bears some humble relationship with the diamond so far as glass-cutting is concerned.

### Microscopical and Natural History Section.

*Ordinary Meeting, January 17th, 1887.*

Prof. W. C. Williamson, LL.D., F.R.S., Vice-President, in the chair.

Mr. R. T. Burnett, F.G.S., was elected an Associate of the Section.

Mr. Henry Hyde exhibited a leaf of *Bryophyllum calycinum*, with young plants growing out of the margin.

Dr. Alex. Hodgkinson read a paper "*On Cavities in Minerals containing Fluid, with Vacuoles in Motion, and other Inclosures.*"

It is matter of common observation that salts in crystallising from their solutions frequently shut off spaces containing portions of the fluid. If at the time of crystallisation the temperature of the liquid was higher than it subsequently comes to be, contraction of the fluid in the enclosed cavity takes place, and a bubble or vacuole is formed. The relative volume of the vacuole to the dimension of the cavity may be taken as a rough indication of the temperature of the solution at the time of crystallisation.

The minerals most commonly containing fluid cavities are quartz (rock crystal, chalcedony, &c.), topaz, emerald, &c. In some specimens of quartz, the milky appearance is entirely due to myriads of minute cavities.

The contained fluid usually consists of either water or an aqueous solution of salts—commonly chloride of sodium. In this latter case crystals of chloride of sodium may often be seen in the fluid. Besides the above, solution of carbonic acid is met with, and even pure liquid carbonic acid.

No. 1 is a specimen of chalcedony from Uruguay, and is chiefly remarkable for the quantity of fluid contained, it being about 60 grains. On shaking, the fluid may be heard to rattle, and the mineral being transparent the bubble

may easily be seen on holding the specimen to the light. Another peculiarity is the absence of any indications of attachment to any other body on the surface of this mineral, rendering its mode of formation a matter of doubt.

No. 2 is a crystal of quartz from Brazil. Three cavities may be seen; one about one-eighth of an inch in diameter contains a viscid fluid, together with a vacuole and an irregular black fragment of mineral matter. Both these are when the specimen is rotated. One of the other cavities contains fluid and a portion of rock magma. In neither of these specimens (1 and 2) can the vacuoles be made to disappear by heat.

No. 3. A piece of rock-crystal containing numerous flattened irregular cavities. Each is seen to contain a flattened vacuole, surrounded by fluid, which fluid is separated from the walls of the cavities by a space which, according to Brewster, contains a second fluid of different optical density. On heating, the vacuole is seen to decrease in size, and finally to disappear. The contour line of the second fluid remains unchanged. On cooling, the vacuole reappears.

No. 4. Section of quartz containing fluid cavities, each containing a crystal of common salt and a vacuole. The vacuoles are motionless and do not disappear on heating.

No. 5. Section of Granite. The fragments of quartz in this specimen abound with minute more or less spherical cavities. Each contains a vacuole which in the large and medium sized cavities may be seen when highly magnified (¼ in.) to rise to the upper part of the cavity when the specimen is rotated. Warming facilitates this, apparently rendering the fluid less viscid. The feature of interest in this specimen is the spontaneous movement of the vacuoles. At ordinary temperature the motion of the largest vacuoles consists in a faintly perceptible throbbing motion; in the medium sized this is increased, while in the smaller cavities the vacuole wanders about its cell with a rapid jerking motion; on applying heat the vacuoles gradually decrease in size, and become more active as they become smaller, until finally, before disappearing, their motion becomes too rapid to follow, but is chiefly confined to the upper part of the cavity. If allowed to cool, the vacuole suddenly reappears of its full volume at the lower part of the cavity, instantly rising to the top. The motion of the smaller vacuoles seems incessant, but I have never observed them at a freezing temperature. If the source of heat, whether a heated metal or glass rod, be applied either on one side or at the upper or lower part of the cavity, the vacuole at once passes to that side, and in this way may be made to pass to any part of its cell by moving the heat source in the desired direction. Whether such movement is an attraction of the vacuole, or a repulsion of its surrounding fluid, is not easy to decide. That it is not due to the nature of the heating body is shown by its occurrence from proximity of any heated substance, whether of glass or metal. The vacuoles in the smaller mineral cavities are interesting as being the smallest isolated portions of gaseous matter observable, and their extraordinarily active movements in a comparatively dense medium seems suggestive of the kinetic theory of matter.

## NOTICES OF BOOKS.

*A Text-Book of Inorganic Chemistry.* By Prof. VICTOR VON RICHTER. Authorised Translation by EDGAR F. SMITH. Second American from Fourth German Edition. Philadelphia: Blakiston, Son, and Co. London: Trübner and Co.

WE learn from the preface to the first edition that the periodic system is "made the basis of the present volume." Such being the case it is the more to be regretted that whilst ample credit is given to Professors Mendeleeff and Meyer, Mr. J. A. R. Newlands is completely ignored. Yet this chemist's priority as regards the main features of the periodic system is established beyond the shadow of doubt. It is surprising that neither Prof. von Richter nor Prof. E. F. Smith has met with the original papers of Mr. Newlands in the CHEMICAL NEWS or in other journals in which they have been reproduced. A prominent feature of this work is the attention paid to thermo-chemistry—a branch of the science too generally overlooked in text-books, though it is acquiring increased importance.

We regret to notice the frequent use of the word "metalloids" for the non-metallic elements.

One very important passage calls for special and—in our opinion at least—most favourable notice. We read:—"The fundamental deduction necessarily resulting from the law of periodicity is, that the various elementary atoms must be aggregations or condensations of one and the same primordial substance, a necessary correlative postulate of the recognised unity of all forces. Then only can we comprehend that the properties of the elements are functions of the atomic weight."

Concerning Prout's hypothesis the author reserves judgment, pending the exact determination of the atomic weights of a majority of the elements. But he duly notes the fact that, of the simple bodies whose atomic weights have been already ascertained with precision, at least one-half closely approximate to the demands of the law.

Had the author of this work been willing to render honour where honour is due, it would merit our almost unqualified commendation. As it is, it will be of great value to the student from the author's successful endeavours to bring fact and theory into harmonious relation.

The index is not unimpeachable.

*Chemistry of the Carbon Compounds; or Organic Chemistry.* By Prof. VICTOR VON RICHTER. Authorised Translation by E. F. SMITH, Professor of Chemistry, Wittenburg College, Ohio. From the Fourth German Edition. Philadelphia: P. Blakiston, Son, and Co. London: Trübner and Co.

PROFESSOR VON RICHTER'S work has the merits of being singularly clear, well-arranged, and, for its bulk, comprehensive. Hence it will, as we find it intimated in the preface, prove useful not merely as a text-book, but as a manual of reference.

In the introduction the author lays due weight on the distinction between *organic* and *organised* bodies. Still, even with this reservation, it seems hazardous to state that "all substances belonging to plants and animals can be artificially prepared from the elements." Most of the artificial organic bodies now so commonly prepared have their starting-point, not in the elements, but in the residues of matter once organised.

As regards the translation the language employed is in some cases open to question. Thus we read (p. 38) "The unsaturated compounds boil some higher than those saturated," and on the next page we find mention of a drawn out tube "fused shut at one end." In speaking (p. 600) of dyeing with indigo, Prof. E. Smith writes:—"the indigo blue is changed by fermentation to indigo white, the weaving saturated from the latter and exposed to the air." Instead of "weaving," the tissue or the cloth would be the ordinary English rendering of the German "Gewebe."

Throughout the book there occur similar peculiarities of expression, which give a jar to the reader's mind, and may make him for a moment doubtful as to the meaning which the translator desires to convey. With a little care these flaws in an otherwise excellent work might have been kept out.

*Illustrated Handbook of Victoria, Australia.* 1886. Melbourne: John Ferres.

THIS most interesting work on the colony of Victoria was specially prepared for the Colonial and Indian Exhibition,

with a view to bringing the capabilities and resources of the country more prominently before the people of older England.

The first expedition to Australia of which any record is left was in the year 1616, and the first settlement was made in January, 1788.

The mineral wealth of Australia is enormous, and the discovery of gold in 1851 had more to do with the rapid rise into importance of the colony than years of "squatting" would have done. Gold is found in two principal formations, viz :—In quartz, and in alluvial beds; the first named is mined in a similar manner to other metalliferous lodes, and after crushing the quartz the gold is separated by means of mercury. Alluvial gold, on the other hand, is generally found with gravel or loose soil, and is separated by washing; full descriptions of both these methods are here given, with the weight and value of the gold produced.

Sheep farming and cattle raising being important branches of industry in Victoria, are also fully treated; wine growing also attracts considerable attention. But what is most striking on looking through this book, is the wonderful progress the colonists have made in beautifying their cities.

At the end of the volume are 74 full page engravings of the principal buildings, streets, public monuments, &c., in this colony, which testify to the energy and perseverance of those who are making a new England for future generations.

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*Report of the Port of London Sanitary Committee :* with the Half-yearly Report of the Medical Officer of Health for the Port of London, to December 31, 1886.

In this last report of the sanitary condition of the Port of London, during the latter half of 1886, Dr. Collingridge is happy in not having to record much sickness of an infectious nature, the whole year having been unusually free from disease of this nature.

Appendix A shows that during the last six months of the year no less than 11,064 vessels of all classes were inspected by the officers of health, 84·44 per cent (that is 9343) being British; of these, 798, or 7·2 per cent, were found to require cleansing of some sort. It is encouraging to note that in such instances the verbal order of the inspector is almost always sufficient, the necessity of further proceedings being very rare, and then only when some special reason exists. Only six vessels have had to be fumigated on account of infectious diseases, a smaller number than in any half year since 1879.

This Committee has not only to deal with the sanitary condition of the vessels arriving in London, but also with the condition of the river on which this port is situated; the problem is a serious and most important one, and although it is some years since the first experiments in this direction were made, we are sorry to see that little or no progress has been made in keeping the river free from contamination with the large amount of sewage which has daily to be disposed of. The uncertainty of our climate, says Dr. Collingridge, always affords a hope that during the summer there will not be a sufficiently long period of hot weather to cause the terrible nuisance to reappear, and unfortunately this uncertainty has been made the most of. The large experiment that the Board of Works are about to spend half a million on is now tolerably well known, but it is hardly to be hoped that much, if any, benefit will result therefrom. During last summer 9 million gallons daily were treated with lime and sulphate of iron, and then, before discharging, with permanganate of soda as a deodoriser. The result was unsatisfactory, except in cool weather, but when in August the temperature rose the river water became foul and discoloured (the natural result of using iron salts) giving off the usual horrible stench. The presence of cholera on the Continent has again attracted the attention of this committee, who have been successful in keeping the Port of London free from that terrible scourge; in commenting on the passage of the "Euphrates" through the Suez Canal while infected with cholera, the writer of this report says, "such a procedure must, of necessity, be a great blow to the dangerous and barbarous system of quarantine," an opinion which we think will be pretty generally endorsed, at least in this country.

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*Bulletins Nos. 5, 6, and 7 of the Louisiana Sugar Experiment Station.* By Wm. C. Stubbs, Ph.D. Baton Rouge, U.S.A., 1886.

These three bulletins deal respectively with the cultivation of sorghum, corn, and sugar-cane. The first and third have been carefully experimented with in order to find the best manure to give a large yield of sugar, while the yield of grain has been the object in the other case. Sorghum has been cultivated in the United States of America and elsewhere for a number of years, and has been used largely as forage for cattle. For nearly thirty years the Americans have been trying to make sugar from it, but in China, where we are told it has been cultivated for thousands of years, there is no evidence that it has ever been used with that view. The origin of sorghum is utterly unknown; its habits and characteristics have been so changed by long cultivation that it cannot be found to resemble any wild plant. These experiments are the first that have been made in a systematic manner, but as yet the success achieved has only been partial; there were three experiment stations, *a*, *b*, and *c*.; *a* was fertilised with ammoniated acid phosphate, *b* was unfertilised, and *c* with ammoniated acid phosphate and a little chloride of potassium.

The results of the analyses, which were made at short intervals, are given in a table. Of the different varieties used the Chinese was the first to ripen, and though rich in sugar it is too small a plant to be profitably worked; Indian sorghum is a fine variety and gave a very good yield; but the variety known as Sink's Hybrid is said to be the best adapted for the production of sugar. The highest individual yield of sucrose was 50 per cent, and was obtained from plot *c*, from the Honduras sorghum, though in most cases the fertiliser used has made little or no difference.

The sugar-cane has been known from time immemorial, but it is believed to have come originally from India; rich soils filled with vegetable matter are best suited to it. The field experiments at the station during the past year were of four kinds, viz. :—

1st. Germination questions.
2nd. Physiological questions.
3rd. Varieties best adapted to Louisiana.
4th. Manurial requirements.

The old question among planters as to which part of the cane should be planted, that is to say, the tops, the entire stalk, or only the matured parts, has been carefully tried; the experiments were, however, to a large extent vitiated by the bad weather, but the best results were obtained from the plot planted with the partially green third and fourth joints from the top of the cane. These experiments will be tried again.

Many persons have long been of the opinion that side shoots which spring up round the base of the original plant, known as "suckers," were very detrimental, on the grounds that they took their nourishment from the centre stalk. This has been found not to be the case, the "suckers" actually increasing the yield of sugar.

Passing over the experiments to decide what variety is the best suited to Louisiana, we come to those on manurial requirements. The first of these experiments made with various quantities of cotton seed, phosphate, kainite, gypsum, "floats" (bone dust and Charleston phosphate), stable manure, &c., shows that a mixture of cotton seed meal and an acid phosphate produces the highest results, that kainite adds nothing to the crop, and that the application of manure in the autumn is as bene-

ficial as when applied in the spring. Phosphoric acid gives an increase in the yield, but after a certain amount the increase is not in proportion to the quantity applied; from this it is very naturally concluded that large quantities are useless and expensive.

The results obtained from the trials with chloride, sulphate, nitrate, and carbonate of potassium, and kainite (sulphate of potash and magnesia) were discordant and very unsatisfactory; for the largest yields came from the unfertilised plots.

The cultivation of corn depends to a very great extent on the locality, corn being essentially a child of the sun, and no fixed rules applicable to all countries can possibly be given. Corn should never be planted until the temperature of the soil one inch below the surface is above 50° F. The rule here given as to the time of planting is a quaint one, viz., "When the leaves of the white oak get as big as a squirrel's ear": this sounds rather vague, the size of a "squirrel's ear" being a variable quantity, but it is said to be correct.

A large number of experiments were tried with different manures, as in the other cases, but the results do not appear to be of much value, owing to depredations made by birds on the one hand and worms on the other.

The director of this station is carrying out a very useful work, but the reports are marred by innumerable printer's errors and mistakes.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

**NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.**

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 7, February 14, 1887.

**Physical Researches on the Isomerism of Position**—Alb. Colson.—The author finds that the three isomeric carbides, paraxylene, orthoxylene, and metaxylene, which present a remarkable parallelism in their chemical reactions are also connected by physical relations, especially if studied calorimetrically.

**Action of Mercury upon Some Chlorides in Solution.**—G. André.—The author examines the behaviour of mercury oxide with calcium, barium, strontium, and magnesium chlorides.

**Action of Hydrochloric Acid upon the Solubility of the Chlorides.**—R. Engel.—The author has shown in a former memoir that the solubility of the chlorides which hydrochloric acid precipitates from their aqueous solutions decreases, in presence of this acid, by a quantity corresponding approximately to an equivalent of chloride for each equivalent of hydrochloric acid added. This law, which is only an approximation, holds good, especially at the outset of precipitation, and in many chlorides three-fourths of the salt in solution are precipitated according to this law. On further examination this fact has been found very general. Metallic chlorides of the most different groups, those whose crystals are anhydrous and those which have water of crystallisation, the very soluble, and the sparingly soluble, follow this law at the outset of their precipitation with hydrochloric acid. No relation appears between the point after which the precipitation of a salt begins to deviate from it, and the other physical and chemical properties of the salt. Similar phenomena are observed in the action of nitric acid upon the solutions of the nitrates. Sulphuric acid behaves quite differently when acting upon the solutions of sulphates with which it does not form acid sulphates.

**Poisonous Character of Colchicine.**—A. Mairet and Combermale.—Colchicine acts as an irritant poison, affecting all the organs, but especially the digestive canal and the kidneys. The minimum fatal dose of colchicine for dogs and cats is 0·000571 grm. per kilo. of the weight of the animal, if introduced hypodermically, but 0·00125 grm. per kilo. if introduced into the stomach. Colchicine is eliminated by different channels, but this process is slow, whence slight but repeated doses, 0·00016 grm. per kilo., may prove fatal in five days.

**New Process for determining the Carbonic Acid given off and the Oxygen Absorbed in Respiration.**—M. Hanriot and Ch. Richet.—The air inspired traverses a gas-meter (I.) which measures its volume. The air expired traverses in succession two meters (I. and II.) between which is placed an apparatus for absorbing carbonic acid. The difference of volume registered between I. and III. gives the volume of oxygen absorbed, and the difference between II. and III. shows the volume of carbon dioxide produced.

No. 8, February 21, 1887.

**Calcium Orthobutyrate and Isobutyrate.**—G. Chancel and F. Parmentier.—The authors show that the generalisation of M. Le Chatelier (*Comptes Rendus*, c., 50 and 441) cannot be considered as the expression of a law from which new and certain deductions may be drawn.

**Red Fluorescence of Aluminium.**—Lecoq de Boisbaudran.—The author has continued his experiments on alumina, which has been ignited at different temperatures with the additions respectively of chromium and bismuth oxides.

**The Determining Causes of the Phosphorescence of Calcium Sulphide.**—A. Verneuil.—The author refers to a former paper (*Comptes Rendus*, ciii., 600) showing that to obtain a calcium sulphide giving a violet phosphorescence it is necessary to calcine a mixture of 100 parts of lime from the shell of *Hypopus vulgaris*, 30 sulphur, and 0·02 bismuth subnitrate. He finds now that the sulphide thus prepared owes its peculiar phosphorescence at once to the salt of bismuth, to sodium carbonate and chloride, and to the calcium sulphate formed during the reaction, and as an increase of the quantities of carbonate of soda and common salt does not notably increase the luminosity of the product, the shell must contain these fluxes in the best proportions for the effect required.

**Action of Certain Metals upon Silver Nitrate in Dilute Solutions.**—J. B. Senderens.—Lead, zinc, iron, cadmium, tin, antimony, aluminium, acting on dilute solutions of silver nitrate, reduce the nitric acid simultaneously with the precipitation of the silver. Corresponding phenomena are observed with other nitrates.

**Action of Sulphuric Acid upon the Solubility of the Sulphates.**—R. Engel.—Certain sulphates do not appear capable of combining with sulphuric acid to form double sulphates. If sulphuric acid is caused to act upon such sulphates, the solubility of the salt diminishes according to a different law from that which holds good for chlorides in contact with hydrochloric acid.

**Reply to a Memoir by M. Boutroux concerning the Action of Nitric Acid upon Sugar.**—E. Maumené.—The author maintains that his hexepic acid is absolutely identical with the oxygluconic acid of M. Boutroux.

**On Sugaring Musts and on the Manufacture of Sugar Wines.**—D. Klein and E. Frechou.—A sealed paper deposited by the authors in October, 1885, and now opened at their request. It treats of the addition of sugar to the juice of imperfectly ripened grapes.

**A Contribution to the Study of the Alkaloids.**—Oechsner de Coninck.—The author has previously shown that if the compounds of the pyridic and quinoleic acids with methyl and ethyl iodides are treated with potassa, very sensitive coloured reactions are produced. He finds that this is not the case with sparteine, which gives merely a rose colour. Nicotin gives a garnet-red colouration, which passes into a carmine and lastly into an orange-yellow. This reaction approximates nicotin to the pyridic and dipyridic alkaloids.

*Justus Liebig's Annalen der Chemie*, Vol. ccxxxvii., Part 2.

The Chloration of Toluol.—E. Seelig.—If dry chlorine is passed, in the dark, into toluol refrigerated with ice, no transferrer of chlorine being present, absorption first takes place, and nothing escapes save unabsorbed chlorine. After some time an escape of hydrochloric acid begins. The green colour of the toluol shows that it always contains notable quantities of chlorine in an unconverted state. Slight elevations of temperature occasion partial transformation and abundant escape of hydrochloric acid. Still more intense is the action of transferrers of chlorine, such as ferric chloride, which cause a brisk effervescence on their introduction. At first, therefore, there ensues merely an addition of chlorine, whilst substitution takes place afterwards.

Oxidation of Symmetrical Trialkyl-pyridin.—Sigm. Altar.—In this memoir the author studies the mono-carbon acids from symmetrical trialkyl-pyridins and their constitution, and the corresponding dicarbon acids.

Researches on Titanium (Second Memoir).—Baron Otto von der Pfordten.—The author's principal results are:—Rutile from St. Yrieux and from Norway always contains vanadium, which will probably be found also in rutile from other sources. This vanadium passes into the purified titanic acid, to which special attention must be given. The yellow compound which persistently clings to titanium chloride is not ferric chloride, but vanadium oxychloride. Hydrated titanic acid may appear in a gelatinous state. Titanium tetrachloride is reduced to dichloride at ordinary temperatures, both by sodium amalgam and by hydrogen sulphide. Titanium dichloride dissolves in alcohol and in water with a deep brown colour, and this relatively permanent solution is precipitated by reagents with formation of titanium monoxide compounds. For this stage of combination potassium sulphocyanide with ether gives a very characteristic and sensitive reaction, *i.e.*, the subnatant stratum becomes colourless, whilst the ether takes a deep brown colour. The solutions of the sesqui-compounds are, according to circumstances, either violet or green. The action of hydrogen upon titanic acid is not a method for preparing titanium sesquioxide, but yields a deep blue compound, $Ti_7O_{12}$. The author considers the preparation of the greatest possible number of compounds and the determination of their permanence essential to an understanding of the elements not yet thoroughly known. In the silicon group a comparison such as he has formerly carried out (*Annalen*, ccxxii., p. 142), is as yet impracticable, since in silicon, zircon, and thorium the lower stages have not been sufficiently studied, the intercalation of cerium is still doubtful, and the character of tin and lead is too different to allow of a useful comparison.

Behaviour of Phosphorus Pentachloride with Substituted Formamides, and on Certain Piperidine Derivatives.—O. Wallach and F. Lehmann.—This memoir does not admit of useful abstraction.

## MISCELLANEOUS.

Phenol-phthaleine Test-Papers.—We have received from Messrs. James Woolley, Sons, and Co. a sample of their new phenol-phthaleine test-papers for detecting an excess of alkali in a solution. One of these papers when placed in a beaker of fluid assumes a bright magenta colour if alkali is present in excess, and on neutralising carefully with acid the colour disappears. These papers will no doubt prove very useful in the laboratory, the reaction being more distinct than that of litmus.

Bronzing of Metals.—Very handsome colours may be imparted to metals, according to *Metallarbeiter*, by the use of cold solutions of the sulphides of arsenic or antimony. The articles are thoroughly cleaned and dried; a thin layer of a dilute solution of polysulphide of ammonium is applied with a soft brush, allowed to dry, and after brushing off the separated sulphur, a dilute ammoniacal solution of sulphide of arsenic is applied. The colour thus produced resembles that of mosaic gold, and becomes deeper and ultimately dark brown by repeating the application of the arsenic solution. A solution of sulphide of antimony produces a rose-coloured tint, which may be deepened to dark red. By polishing, the coating acquires a bright metallic lustre, and by the use of mordants the colour is altered. Brass or bronze left for a long time in contact with the mordant becomes superficially greenish grey, and quite glassy on being polished with cloth; if now treated with the above solutions a dull yellow colour is produced. The bronzing layer may be re-dissolved by ammonia or sulphide of ammonium, and the sulphides of antimony and arsenic may be dissolved in hydrate or sulphide of potassium or sodium.—*American Journal of Pharmacy*.

The Chemical Laboratory of Wiesbaden.—The Chemical Laboratory of Geh. Hofrath Prof. Dr. Fresenius at Wiesbaden enjoys a very large attendence. In the winter term, 1886-87, there were 77 students on the books. Of these, 53 were from Germany, 5 from England, 5 from North America, 4 from Austria, 3 from Russia, 2 from Belgium, 2 from Italy, 1 from France, 1 from Spain, and 1 from Sumatra. Besides the Director, Geh. Hofrath Prof. Dr. R Fresenius, there are engaged as teachers in the establishment Prof. Dr. H. Fresenius, Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. F. Hueppe, and Architect Brahm. The assistants in the instruction laboratory were two in number, in the Versuchsstation three. During the last term, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory and the Versuchsstation on behalf of manufacture, trade, mining, agriculture, and hygiene.

Jubilee Exhibition at the School of Science of the City and County of Lincoln.—The friends of science are requested to favour this new, handsome, and important scientific college with the loan of anything of interest in the physical and natural sciences, such as rare scientific works, specimens of minerals, crystals, rare metals, models of chemical plant and machinery, inventors' apparatus, or original specimens of chemicals, &c. The President of the Exhibition is the Right Hon. Earl Brownlow, and the Committee include, amongst numerous others, the Most Hon. Marquis of Ripon, Earl Yarborough, Viscount Oxenbridge, Lord Bishop of Lincoln, His Honour Judge Stephen, LL.D., Dean of Lincoln, Mr. Chaplin, M.P., Mr. Kerans, M.P., Mr. Waddy, Q.C., M.P., Right Hon. E. Stanhope, M.P., Right Hon. E. Heneage, M.P., the Mayors of Lincoln, Grantham, Boston, Grimsby, Louth, and Stamford, Dr. A. B. Griffiths, F.R.S. (Ed.). A guarantee fund to indemnify the General Committee amounts to far over £1000, and will be doubled if necessary. Intending exhibitors can obtain forms and full information from Dr. Griffiths, School of Science, Lincoln. The Exhibition opens on June 22nd, but all intending exhibitors are requested to make application before April 31st next. This Exhibition is intended to be the "ornamental opening" of the new buildings of the Science School of Lincoln. After June 22nd, they will be known as the "Victoria School of Science of the City and County of Lincoln."

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Hard Water and Stone.—I shall be obliged if any one can inform me if there are any statistics published showing any connection between the prevalence of stone and the hardness of the water supply

I have heard it stated that stone is most frequent in hard water districts. Is there any truth in this statement, or does the accretion depend upon personal idiosyncracy? I once knew a man at Market Harbro' who passed a stone from the kidneys, and he declared it was entirely due to the hard water In my own district lives a man who is in the habit of indulging in this habit, and yet the water is not very hard—about 12°. I have lately analysed a water (from Worcestershire) which has a total hardness of 42°, permanent hardness 30°. I felt bound, in my report, to mention that hard water has been *accredited* with the power of forming deposits in the system, but that this is a medical rather than a chemical question, concerning which, I believe, doctors differ.—Sm.

## MEETINGS FOR THE WEEK.

Monday, 21st.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "Machines for Testing Materials, especially Iron and Steel," Prof. W. C. Unwin, F.R.S.
Tuesday, 22nd.—Institution of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.
—— Royal Institution, 3. "Function of Respiration," by Prof. Arthur Gamgee, F.R.S.
Wednesday, 23rd.—Society of Arts, 8. "Some of the Conditions affecting the Distribution of Micro-Organisms in the Atmosphere," by Dr. Percy Frankland.
—— Geological, 8.
Thursday, 24th.—Royal, 4 30.
—— Royal Institution, 3. "The Science of Thought," by Prof. F. Max Müller,,M.A., LL.D.
—— Royal Society Club, 6.30.
—— Telegraph Engineers, 8.
Friday, 25th.—Royal Institution, 9. "Colours of Thin Plates," by the Right Hon. Lord Rayleigh, M A., F.R.S.
—— Society of Arts, 8. "Indian Coffee," by Frederick Clifford.
—— Quekett Club, 8.
Saturday, 26th.—Royal Institution, 3. "Sound," by the Right Hon. Lord Rayleigh.
—— Physical, 3. "On the Production of the Finest Fibres," by Mr C. V. Boys. "On Delicate Calorimetrical Thermometers," and "On the Expansion of Thermometer Bulbs under Pressure," by Prof. Pickering.


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### LECTURES.

| | |
|---|---|
| Experimental Chemistry (Inorganic | Prof. H. FRESENIUS, Ph.D. |
| Experimental Physics .. .. .. .. | W. FRESENIUS, Ph.D. |
| Stöchiometry .. .. .. .. .. .. | |
| Organic Chemistry.. .. .. .. .. | E. HINTZ, Ph.D. |
| Chemical Technology .. .. .. .. | E. BORGMANN, Ph.D. |
| Microscopy, with exercises in Microscopic work .. .. .. .. .. .. | |
| Chemistry and Analysis of Foods .. | Prof. H. FRESENIUS, Ph.D. E. BORGMANN, Ph.D. W. FRESENIUS, Ph.D ,and E. HINTZ, Ph.D. |
| Hygiene .. .. .. .. .. .. .. | Dr. med F. HUEPPE. |
| Practical exercises in Bacteriology.. | |
| Technical Drawing, with exercises .. | F. BRAHM. |

The next Session commences on the 25th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. Kreidel's Verlag, at Wiesbaden, or to the undersigned.

Prof. R. FRESENIUS, Ph.D.

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THE CHEMICAL NEWS.

Vol. LV. No. 1426.

## ON RADIANT MATTER SPECTROSCOPY:—EXAMINATION OF THE RESIDUAL GLOW.*

By WILLIAM CROOKES, F.R.S., V.P.C.S.

(Concluded from p. 121).

The different action of calcium, barium, and strontium on the constituents of yttrium is an additional proof, if confirmation be needed, that the bodies I have provisionally called Gα, Gβ, Gδ, &c.,† are separate entities. It may be as well here to collect together the evidence on which I rely to support this view. I will take the bodies *seriatim*:—

Gα.—An earth phosphorescing with a blue light, and showing in the spectroscope a deep blue line, of a mean wave length 482. This earth occurs in different proportions in purified yttria from different minerals. Samarskite, gadolinite, hielmite, monazite, xenotime, euxenite, and arrhenite contain most Gα, whilst fluocerite and cerite contained notably less of this constituent. The addition of lime brings out the phosphorescence in Gα in advance of that of the other constituents. The behaviour in the phosphoroscope of Gα when mixed with the alkaline earths also points to a difference between it and its associates. With lime the blue phosphorescent band of Gα comes into view at a very low speed, the order of appearance with a small quantity of lime being Gβ, Gα, Gδ, and with a large quantity of lime, Gδ, Gα, Gβ. Employing strontia instead of lime the order of appearance in the phosphoroscope when the quantity of strontia is small is Gβ, Gα, Gη, and when the quantity of strontia is in excess, Gα, Gη, Gβ. Baryta in small quantity brings out the lines in the phosphoroscope in the following order, Gβ, Gα, Gη, but when the baryta is in excess the order is Gβ, Gη, Gα. The chemical position taken up by Gα in the fractionation ccheme precludes it from being due to the bodies I have salled Gβ, Gγ, Gε, Gζ, Sγ, or Sδ. It closely accompanies Gδ (the earth giving the citron line), concentrating at the least basic end, and I have not yet succeeded in effecting a separation of the two. If, therefore, Gα is not a separate entity, its blue line must be due to the citron-band-forming body called Gδ. The difference between Gα and Gδ is brought out in a marked manner by the phosphoroscope when baryta or strontia is present; the citron line of Gδ being entirely suppressed, while the blue line of Gα is brought out with enhanced brilliancy. For these reasons I am inclined to regard Gα as a separate body, although the evidence in favour of this view is not so strong as in the case of some of its other associates.

Gβ.—An earth phosphorescing with green light and showing in the spectroscope a close pair of greenish-blue lines of a mean wave length of 545. This earth can be separated by chemical fractionation from the other constituents of yttrium. It concentrates at the most basic end, and is present in the samarium which invariably makes its appearance at this end of the fractionation of yttrium. It is one of the prominent lines in Yα, where also it accompanies some of the samarium lines. Gβ, however, is not a constituent of samarium, for it is easy to purify samarium by chemical means so that it does not show a trace of the Gβ green lines, although it is very difficult to get Gβ free from some of the samarium lines. The residual phosphorescence of Gβ is very considerable, and its green lines show first in the phosphoroscope when only yttrium is present. The addition of lime keeps back the glow of Gβ and brings forward that of Gδ. Strontium and barium act on Gβ very differently to lime. A small quantity of strontium brings forward the residual glow of Gβ, whilst in large quantities strontium keeps the phosphorescence of Gβ back to the last.

Gγ.—An earth phosphorescing with a green colour and showing in the spectroscope a green line having a wave length of 564. This is one of the least definite of all the supposed new bodies. It appears to be a constituent of samarium, occurring in the fractionation of yttrium among the most basic constituents connecting yttrium and samarium. Its point of maximum intensity is, chemically, very well marked, and is at a different part of the fractionation scheme to those of the other lines of samarium, especially Gε. On dilution with lime the phosphorescent line of Gγ vanishes before that of Gε.

Gδ.—An earth phosphorescing with a citron coloured light and showing in the spectroscope a citron line having a wave length of 574. Gδ is one of the least basic of all the bodies associated in yttrium, occurring almost at one extremity of the fractionation. It is not very difficult to separate chemically Gδ from all the other accompanying bodies except the one which I have called Gα (giving the deep blue line). Not only can Gδ be obtained free from the other four constituents of yttrium, but the body called by M. de Marignac Yα is a proof that the other four components of yttrium can be obtained quite free from Gδ. Lime intensifies the phosphorescence of Gδ, and deadens that of Gβ, while strontium has the opposite action. The behaviour of Gδ in the phosphoroscope, when mixed with lime, strontia, or baryta, also affords a striking evidence of individuality; lime enhancing the residual glow, while strontia and baryta altogether suppress it.

Gε.—An earth phosphorescing with a yellow colour, and, in the spectroscope, showing a sharp yellow line having a wave length of 597. It is seen in the samarium spectrum as a sharp yellow line superposed on a hazy double band. As I have already pointed out, Gε fractionates out high up among the most basic earths and generally accompanies lanthanum. In the phosphorescent spectrum of lanthanum the line of Gε is seen quite free from the lines of other bodies.

Gζ.—An earth phosphorescing with a red light, showing in the spectroscope a red line of wave length 619. This body is always more plentiful in yttrium obtained from samarskite and cerite than from gadolinite, hielmite, and euxenite, and is almost absent in yttrium from xenotime. Gζ is of about intermediate basicity. Working with samarskite yttria, Gζ becomes most brilliant after the line of Gη has completely disappeared. Further fractionation causes the line of Gζ to fade out, and the citron and blue lines are then left.

The phosphorescence of Gζ is developed to a different extent according to the metal with which the yttria is mixed. The order (beginning with the substance having the greatest action) is zirconium, tin, aluminium, bismuth, glucinum.

Gη.—An earth phosphorescing with a deep red light, and showing in the spectroscope a red line having a wave length of 647. Like its fellow red constituent, Gη occurs most plentifully in samarskite yttrium, and scarcely at all in yttrium from hielmite, euxenite, and cerite. It is the first of the strictly yttrium constituents to separate out, on fractionation, at the most basic extremity, leaving Gα, Gβ, Gδ, and Gζ. In almost all samples of yttria, except when very highly purified, Gη is seen very brilliantly, and by its side can be detected the faint red band of samarium. In the phosphoroscope the line of Gη is the last to appear when yttria alone is being observed; strontia and baryta enhance the residual glow of Gη, strontia in moderate quantities bringing it out before that of Gβ, while baryta brings it out after Gβ.

Sδ.—An earth giving in the spectroscope when phosphorescing a very sharp orange line of wave length 609. I have already* discussed the claims of this earth to be

* A Paper read before the Royal Society, Feb. 17, 1887.

† *Roy. Soc. Proc.*, vol. xl. (1886), p. 502.

* *Roy. Soc. Proc.*, vol. xl. (1886), p. 504.

considered a separate entity. It is not present in the rare earths from gadolinite, xenotime, monazite, hielmte, euxenite, and arrhenite; it is present in small quantity in cerite, and somewhat more plentiful in samarskite. In samarskite yttrium it concentrates at a definite part of the fractionation. Its sharp orange line is not strong enough to be seen in the phosphoroscope. A little calcium entirely suppresses the orange line, while samarium or yttrium seems to intensify it.

In addition to the above earths, it is not improbable that the sharp green line $\left(\frac{1}{\lambda^2}\ 325\right)$ mentioned under the heading "Yttrium" may be caused by still another earth.

The brilliant and characteristic spark spectra yielded when certain elements are volatilised and rendered incandescent by the spark from a powerful induction coil are relied on by chemists as an indisputable proof of the identity of such elements. Bearing this in mind I have endeavoured to ascertain how these yttrium constituents would behave in respect to the spark spectrum. Do the definite system of lines in the old yttrium spark spectrum belong to one constituent only, or are the yttrium lines broken up and distributed among the different bodies I have designated as $G\alpha$, $G\beta$, &c.? Also do the other constituents possess special spark spectra of their own? Very careful and long continued experiments have shown me that neither of these hypothetical cases occur.

The spark spectrum given by old yttrium is shown in the drawing (Fig. 5). It is chiefly characterised by two very strong groups of lines in the red and orange. I now take the earth $G\delta$. This occurs near one end of the fractioning, and not only differs from the parent yttrium in its phosphorescent spectrum, but by virtue of the process adopted for its isolation it must likewise differ in its chemical properties. On examining its spark spectrum I see absolutely no difference between this spectrum and the one given by old yttrium.

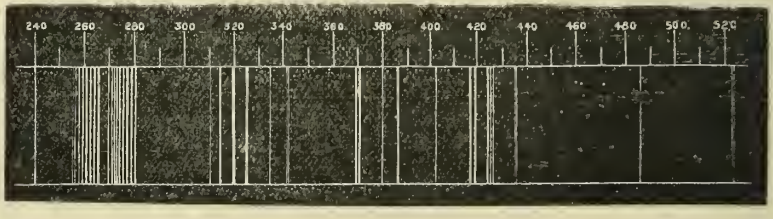
I now pass to the other end of the fractionation of yttrium, where occurs a concentration of a body giving a totally different phosphorescent spectrum to the one at the first end. And it also differs chemically from old yttrium, and in a more marked manner from its brother, $G\delta$, at the other extremity of the fractionation. Here again its spark spectrum is perfectly identical both with old yttrium and with $G\delta$, and however closely I examine these three spectra in my laboratory, the whole system of lines is still identical.

Respecting the theoretical considerations involved in these results, I see two possible explanations of the facts brought forward. According to one hypothesis research has somewhat enlarged the field lying between the indications giving by ordinary coarse chemistry and the searching scrutiny of the prism. Our notions of a chemical element have expanded. Hitherto the molecule has been regarded as an aggregate of two or more atoms, and no account has been taken of the architectural design on which these atoms have been joined. We may consider that the structure of a chemical element is more complicated than has hitherto been supposed. Between the molecules we are accustomed to deal with in chemical reactions and the ultimate atoms, come smaller molecules or aggregates of physical atoms; these sub-molecules differ one from the other, according to the position they occupied in the yttrium edifice.

An alternative theory commends itself to chemists, to the effect that the various bodies discussed above are new chemical elements differing from yttrium and samarium in basic powers and several other chemical and physical properties, but not sufficiently to enable us to effect any but a slight separation. One of these bodies, $G\delta$, gives the phosphorescent citron line, and also the brilliant electric spectrum. The other seven do not give electric spectra which can be recognised in the presence of a small quantity of $G\delta$, whilst the electric spectrum of $G\delta$ is so sensitive that it shines out in undiminished brilliancy even when the quantity present is extremely minute. In the process of fractionation, $G\alpha$, $G\beta$, $G\delta$, &c., are spread out and more or less separated from one another, yet the separation is imperfect at the best, and at any part there is enough $G\delta$ to reveal its presence by the sensitive electric spark test. The arguments in favour of each theory are strong and pretty evenly balanced. The compound molecule explanation is a good working hypothesis, which I think may account for the facts, while it does not postulate the rather heroic alternative of calling into existence eight or nine new elements to explain the phenomena. However, I submit it only as an hypothesis. If further research shows the new element theory is more reasonable, I shall be the first person to accept it.

Neither of these theories agrees with that of M. Lecoq de Boisbaudran, who also has worked on these earths for some time. He considers that what I have called old yttrium is a true element, giving a characteristic spark spectrum, but not giving a phosphorescent spectrum *in vacuo*. The bodies giving the phosphorescent spectra he considers to be impurities in yttrium. These he says are two in number, and he has provisionally named them $Z\alpha$ and $Z\beta$. By a method of his own, differing from mine, M. de Boisbaudran obtains fluorescent spectra of these bodies; but their fluorescent bands are extremely hazy and faint, rendering identification difficult. Some of them fall near lines in the spectra of my $G\beta$ and $G\delta$. At first sight it might appear that his and my spectra were due to the same bodies, but, according to M. de Boisbaudran, the chemical properties of the earths producing them are widely distinct. Those giving phosphorescent lines by my method occur at the yttrium extremity of the fractionation, where his fluorescent bands are scarcely shown at all; whilst his fluorescent phenomena are at their maximum quite at the terbium end of the fractionation, where no yttrium can be detected even by the direct spark, and where my phosphorescent lines are almost absent.

Fig. 5.

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Action of Heat upon Heptene.—Adolphe Renard.—Heptene, under the influence of heat, is decomposed principally into toluene and hydrogen, whilst a certain quantity of its lower homologues, hexene and pentene, are simultaneously formed. The benzine is doubtless derived from a partial destruction of the hexene.—*Comptes Rendus*, civ., No. 9.

ON THE

# BEHAVIOUR OF ALKALINE SOLUTIONS OF PHENOL-PHTHALEIN IN THE PRESENCE OF ALCOHOL.

By HARRY NAPIER DRAPER, F.C.S., and CARTER DRAPER.

## Part I.—Ammonia and Phenol-Phthalein.

THE observation which led to the following enquiry was made by one of us about two years ago. Some methylated spirit, supposed to contain ammonia, having been tested with phenol-phthalein with negative result, the experiment was repeated with alcohol to which aqueous ammonia had been added. *The liquid remained colourless.* This phenomenon was so unexpected and remarkable, and so obviously demanded explanation, that a series of experiments was begun, the deductions from which, simple as they now appear, have often been so baffling and enigmatical as to necessitate digressions from the experimental method at first laid down. As, however, these digressions have led to an extension of the field of enquiry, and the inclusion in it of the deportment of phenol-phthalein with the hydrates of potassium and sodium when alcohol is present, we cannot feel that they are to be regretted.

Phenol-phthalein ($C_{20}H_{14}O_4$) is, as might be inferred from the analogy of its constitution to that of fluorescin ($C_{20}H_{14}O_6$), a weak acid. Baeyer indeed points out that it forms unstable salts.

The same chemist notes that the colour of solutions of these salts is destroyed by excess of caustic alkali and is restored by addition of acid (to partial neutralisation). Also that when a solution of phenol-phthalein in ammonia is boiled, the ammonia is expelled and the phenol-phthalein separates.*

But why should the addition of alcohol to an ammonia solution of phenol-phthalein destroy its colour? Baeyer and Burkhardt† have pointed out that aqueous ammonia at high temperatures acts readily upon phenol-phthalein, forming a compound, di-amidophthalein, which crystallises in colourless needles, and to which they assign the constitution—

$$C_6H_4\begin{cases}C.NH.C_6H_4.OH\\C.NH.C_6H_4.OH.\end{cases}$$

Long, in an excellent paper‡ on the interference of salts of ammonia with the phenol-phthalein colour reaction in volumetric analysis, explains it on the hypothesis that with nascent ammonia the imido compound would probably be formed at ordinary temperatures, and his observation, that the decolouration is more rapid as the temperature of the liquid is higher, supports this theory; indeed phenol-phthalein in presence of concentrated aqueous ammonia is quite readily converted in a few days, at 40° C., into the imido compound.§

At first sight, therefore, it did not appear unreasonable to suppose that alcohol, by its affinity for water, played the part of time or heat, and caused a weak ammonia solution to behave like a stronger and non-alcoholic one. But an objection fatal to this theory soon presented itself. A solution of di-imidophthalein remains colourless when diluted with water to any extent, while the colourless compound formed in alcohol has its colour at once restored on addition of water. It was obvious, then, that some other cause for the phenomenon must be sought out.

In order that experiments made with this object might be comparable among themselves, two standard solutions were prepared as follows:—

| | |
|---|---|
| Phenol-phthalein .. .. .. | 1 grm. |
| Absolute alcohol .. .. .. | 100 c.c. |
| $NH_4OH$ .. .. .. .. .. | 1 grm. |
| Water .. .. .. .. .. | 100 c.c. |

If equal volumes of these solutions be mixed, the coloured mixture is rendered colourless by addition of alcohol. The mean result of several experiments gave the quantity of alcohol required for 1 c.c. of each solution, at a temperature of 10°, as 3·1 c.c. If to the decolourised liquid water be added, the colour is again restored, to be again destroyed by addition of alcohol and restored once more by further addition of water. If the alcohol used be *boiled* before its addition to the coloured liquid, a considerably greater quantity is required—the temperature being the same—than in the case of unboiled alcohol. For example, in one experiment at 12° C., where 10 c.c. of each of the standard solutions were employed, the quantity of previously boiled alcohol required to effect decolouration was 40 c.c., while of unboiled alcohol 31 c.c. were sufficient to destroy the colour.* When to the solution decolourised by alcohol just sufficient water is added to restore the colour, it is at once rendered colourless by a very gentle heat. The colour returns on cooling, and the result is the same whether the experiment be made in a closed or in an open tube. The temperature required to effect decolouration varies so strikingly for each proportion of alcohol and water as to suggest the possibility of founding an approximate alcoholometric method upon the reaction. This itself is most easily demonstrated when, to equal volumes of phenol-phthalein and ammonium solutions of the above indicated strength, enough alcohol or ordinary rectified spirit is added to cause decolouration, and then just as much distilled water as is sufficient to produce a distinctly red tint.

The facts so far ascertained so clearly pointed to a dissociating action exerted by the alcohol, that the inference that the anhydrous compound of phenol-phthalein formed at ordinary temperatures is colourless, seemed unavoidable. That this inference is correct is, we think, demonstrated by the two following experiments:—

(*a.*) Bibulous paper (which had been previously prepared by treatment with dilute hydrochloric acid and repeated washing with distilled water) was dried at 100°, moistened with a solution of phenol-phthalein in alcohol, and again dried. This paper, when exposed to the action of ammonia vapour, remained uncoloured.

(*b.*) Paper prepared as above, and enclosed in an atmosphere of dry ammonia in a sealed tube for ten weeks, remained colourless; but at the end of this time, on being moistened with distilled water, became intensely red.

The phenomenon of decolouration by heat and restoration of the colour by cooling, of a weak ammonia phenol-phthalein solution to which not quite enough alcohol has been added to destroy the colour, may, if a sealed tube be employed, be repeated almost indefinitely. A mixture of—

| | |
|---|---|
| Standard phenol-phthalein .. | 10 c.c. |
| Standard ammonia .. .. .. | 10 ,, |
| Alcohol .. .. .. .. .. | 5 ,, |

fulfils exactly the necessary conditions. A sealed tube containing this solution may be heated to 100° for half an hour, but that in this time and under these circumstances the colourless di-imido compound is not formed is shown by the complete return of the colour when the tube is cooled. But how far the heating of a liquid in which phenol-phthalein, ammonia, and alcohol bear these proportions, can be continued without permanent loss of colour we are unable to say, for after a more lengthened heating the liquid in the tube becomes permanently coloured. This at first puzzling reaction was, however,

* *Deut. Chem. Ges. Ber.*, xi., 1297, and *Journ. Chem. Soc.*, xxxiv., p. 866.

† *Journal of the Chemical Society*, vol. xxxviii., p. 653; and *Annalen*, ccii., pp. 36—140.

‡ CHEMICAL NEWS, li., p. 160.

§ Long's note, that partial neutralisation by an acid restores the colour, does not, however, point to the presence of the imido compound, which is not affected by acids.

* This fact—simply noted here, and not affecting the phenomena immediately under consideration—will later on be seen to acquire important significance.

finally found to be due to the solvent action of the liquid on the tube itself and the formation of a coloured sodium salt of phenol-phthalein. This was demonstrated by a number of experiments in which the ammonia was omitted from the solution, which, when heated in a sealed tube for an hour at 100°, became temporarily and slightly, but in from three to four hours strongly and permanently, coloured. Perhaps no experiment could be devised which would exhibit more strikingly than this, and at one and the same time, the solubility of ordinary glass at comparatively low temperatures, and the sensitiveness of phenol phthalein as a reagent.

We conclude, then, that the action of alcohol upon a dilute ammoniacal solution of phenol-phthalein is one of dissociation; that the loosely combined ammonia salt is, when anhydrous, colourless; and that alcohol, in decolourising it in its hydrated form, plays precisely the same part as when, in proportions alike dependent upon the amount of water present and the temperature employed, it converts into the blue anhydrous salt the cobalt chloride of a red aqueous solution.

(To be continued.)

## LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 28TH, 1887.

By WILLIAM CROOKES, F.R.S.,

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

and C. MEYMOTT TIDY, M.B., F.C.S.,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

*To* COLONEL SIR FRANCIS BOLTON, *Water Examiner, Metropolis Water Act*, 1871.

London, March 7th, 1887.

SIR,—We submit herewith the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from February 1st to February 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

The condition of the supply of water to the Metropolis during the past month, in respect more particularly to its degree of freedom from turbidity, has been far more satisfactory than it was during the month of January; when, owing to the occurrence of a sharp frost, supervening on floods brought about by the thawing of a heavy snowfall, the action of the filter-beds in general was much impaired just when most called upon, with the result of more or less turbidity being met with in some portion of the first fortnight's supply of water. During the past month no sample of Thames-derived water has been found otherwise than clear and efficiently filtered; while only one sample of Lea-derived water, out of the total 168 samples of water examined, has had to be recorded as "very slightly turbid." In respect also to its smaller proportion of organic matter, and more complete freedom from brown tint of colour, the supply of last month has shown a decided improvement; although indeed the proportion of organic matter present even in the January supply was not excessive for the time of year.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

## THE ADULTERATION OF OILS.

By THOMAS T. P. BRUCE WARREN.

ANYONE who has paid much attention to the matter of oils must feel that we can hardly congratulate ourselves when we consider how little has been done, during the last twenty years, to render our knowledge of this very important subject more complete and trustworthy.

With a few trifling exceptions, indeed, all that appears from time to time in our chemical journals may be found in Chateau's "Corps Gras Industriels" (1864) and Fontenelle's "Manuel d'Huiles" (1866).

The following is taken from the *Standard* of the 7th inst., on the authority of their New York correspondent:—"The American Cotton-seed Oil Trust Corporation, whose capital is not publicly known, but is supposed to be about thirty or forty millions of dollars, monopolises the business after the methods of the Standard Oil Company; so that when, within four days, the stock fell from sixty-three to forty-two, the matter became one of world-wide importance. It appears that American lard, which is exported everywhere, is largely adulterated with cotton-seed oil. Messrs. Armour and Co., of Chicago, say they use one fifth of the entire product in packing their lard. As the Trust held its oil 100 high, and even projected packing lard itself, the Armour Company is starting its own cotton-seed mills. A repetition of the oleo-margarine frauds appears not unlikely."

This announcement is such a glaring insult to the forensic talent of our analysts that I cannot longer refrain from publishing the value of a new reagent which is likely to be largely adopted.

In the manufacture of oleo-margarine in this country cotton-seed oil is more largely used than many would believe; hence English lard oil may not unreasonably be suspected of coming under the same category as the American.

A few months ago I had occasion to examine some samples of lard oil, both English and American. I had reason for pronouncing the American as adulterated with over 50 per cent of cotton-seed oil, and the English with about 25 per cent. More recently I have examined an American oil, and am able to speak a great deal more favourably on it. If adulterated at all, it is certainly not mixed with cotton-seed oil; so far I accept this as genuine lard oil.

Since lard oil is largely used as a lubricator, and is nearly double the price of cotton-seed oil, it is a matter of great importance to be able to detect its adulteration with cotton-seed oil.

Lard oil itself does not turn green so easily when placed in metal cups, as brass, bronze, &c., but if mixed with cotton-seed oil its action is very soon perceptible. The temperature at which a mixture of these two oils becomes pasty, as compared with lard oil, will give a fair idea of what may be expected in the quantity of adulterant.

If cotton-seed oil has been thickened by partial oxidation (blowing air through the heated oil), it may mislead one in arriving at a conclusion in this way, but in such a case its rapid action on metals is more pronounced.

So far as my observation has extended, all oils which have a tendency to thicken are acted upon by chloride of sulphur, and it is by means of this substance, when diluted

with bisulphide of carbon or petroleum ether, that I separate one class of oils from the other.

Cotton seed oil was at one time largely exported to Italy from this country for adulterating olive oil. This I believe is now replaced by sesame oil, and which—being an easily vulcanisable oil—is more readily detected than cotton-seed oil, with chloride of sulphur.

I may state here that oils which are affected by chloride of sulphur are unequally acted on by this reagent; but this I propose to consider in detail, at a future time.

A short time ago I was informed by a firm of oil brokers that there was no sesame oil in the market! In France sesame oil has been used for cooking purposes for some years past: there is no doubt but that it is wholesome and nourishing; this, however, hardly justifies our paying five shillings per gallon for olive oil if adulterated with sesame oil, which can be bought for about 2s. 6d. per gallon at Dunkirk.

I have at present a broker's prices-current of oils laying before me, in which olive oil is quoted at 5s. per gallon *for eating*, and 2s. per gallon for another quality of the same oil. I have known it supplied recently at 1s. 8d. per gallon.

I am painfully convinced that our oil experts are not aware of the license extended to dishonesty by too explicit a reliance on antiquated methods of research, and it is in the hope of giving prominence to this matter that I somewhat reluctantly publish this information,—I say *reluctantly*, because I am convinced dishonest practitioners will only give up one fraudulent practice for another more likely to give trouble in its detection.

The present use of cotton-seed oil and sesame oil as adulterants in the cases alluded to betrays an amount of ignorance which is simply appalling.

Castor oil, which is not regarded as a drying oil, is violently affected by chloride of sulphur; in such cases the chloride should be more largely diluted with bisulphide of carbon.

When oils are acted upon with this reagent they are converted into solid, easily pulverulent masses, from which the unconverted oil may be removed by bisulphide of carbon. On evaporating this solvent the amount of unaltered oil is obtained.

With lard oil a few precautions are necessary, but of this more will be said on a future occasion.

I can only say that anyone who has once witnessed this reaction will not readily forget the peculiar change, yet, strange to say, this reaction formed the subject of a patent by Alexander Parkes as far back as 1846.

The writer in 1871 patented the manufacture of similar compounds by melting sulphur with these oils. The resulting compound I termed "theionoline."

I am happy to say that an analyst of experience in these matters has kindly consented to work up this method of examining oils, for I am convinced that our present methods of analysis are defective, and consequently the fraudulent manufacturer is allowed to offer his "mixings" without a word being said to sober down his notions of "caveat emptor."

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, March 17th, 1887.*

Dr. Hugo Müller, F.R.S., President, in the Chair.

Messrs. Hugh Robert Mill, Gerald T. Moody, and Arthur Stanley were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William C. T. Beasley, Honiton School, Devon; Edwin Richardson Blundstone, B.A., 10, Wellington Mansions, Regent's Park, N.W.; Samuel Francis Burford, Halford Street, Leicester; Henry Danber, Kenmore, Waterloo Park, near Liverpool; William Gregory, Trent Valley Brewery, near Lichfield; T. O. Sandell, 1, Baron's Court Road; Leonard Owen Simmons, Fareham, Hants; Samuel Sutcliffe, Mostyn, North Wales.

The following were elected Fellows of the Society:—Messrs Harold G. Colman, James T. Cundall, Alfred J. Evans, Arthur Harden, William Houlding, Theophilus H. Redwood, George Robertson, W. H. Stanger, Patrick T. O'Sullivan.

The following papers were read:—

26. "*The Action of Heat on Nitrogen Peroxide.*" By Dr. A. Richardson, University College, Bristol.

The dissociation of nitrogen peroxide has been investigated by Deville and Troost, and other experimenters, at temperatures between $-12°$ and $180°$; and it has been shown that while at low temperatures the molecule of the substance is represented by the formula $N_2O_4$, dissociation into nitrogen dioxide, $NO_2$, takes place with rise of temperature, being complete at 140°.

Experiments have been made by the author to determine the change which takes place at temperatures above 140°. On heating the peroxide at about 500° the gas becomes nearly colourless, and is found to consist of nitric oxide and oxygen; the presence of the former being indicated by the formation of the dark blue liquid which results from the interaction of nitric oxide with nitrogen peroxide when the gas is condensed, and the presence of oxygen being demonstrated by the re-kindling of a glowing match.

At a temperature at which decomposition is complete the change would be represented by the equation—

$$2NO_2 = 2NO + O_2;$$

the vapour-density of the dioxide being 0·23, that of the product is 15·3. On determining the density of the gas at temperatures between 130° and 500°, the numbers obtained were in agreement with the formula $NO_2$ at 140°, but as the temperature rose they more and more nearly approached that corresponding to complete dissociation. The curve representing the density of the gas at different temperatures shows that the decomposition of $N_2O_4$ into $NO_2$ is complete at 140°, and is immediately succeeded by the further dissociation of nitrogen dioxide into nitric oxide and oxygen. The form of the curve is that usually exhibited by dissociating substances, the change of density being most rapid at the temperature at which half the total number of molecules of the original substance are decomposed.

27. "*Supersaturation of Salt Solutions.*" By W. W. J. Nicol M.A., D.Sc.

This paper contains an account of experiments on the physical constants of supersaturated and dilute salt solutions. The solutions were examined in two ways: 1st, concentration constant and temperature varying; 2nd, temperature constant and concentration varying: in this way it was possible to pass from dilute to supersaturated solutions, and to examine the change in the various physical constants. The electric conductivity, specific viscosity, and rate of expansion were examined by the first method; the specific viscosity and density by the second. In every case it was found that the curve corresponding to the non-saturated solutions was perfectly continuous with that for the supersaturated solutions. From this the author concludes that the constitution of dilute, saturated, and supersaturated solutions is the same. Supersaturation is explained by the hypothesis that the substance in solution is not the same as that which crystallises out. A supersaturated solution of sodium thiosulphate deposited crystals of the composition $Na_2S_2O_3H_2O$ when evaporated *in vacuo*, showing that the solution does not contain the pentahydrate. The author believes that the salt in solution is combined with the whole of the water, an opinion based on his experiments on vapour-pressures and molecular volumes. Colour

changes in solution are not, he believes, due to hydration, but to re-arrangements of the salt molecule similar to that which occurs in the case of chromium sulphate.

Discussion.

Mr. Pickering said that he could not agree with Dr. Nicol in concluding that a supersaturated and non-supersaturated solution have identical constitutions, or that the salt was not combined with the solvent. A large number of the physical properties of solutions, such as the volumes of the dissolved salt, the lowering of the freezing-point, &c., appear not only to afford no evidence of the existence of combination between the salt and the solvent, but would even, if taken alone, show that the radicles composing the salt itself are not combined; it was only by taking into consideration all the properties of solutions that we could obtain a correct conception of their nature. When examined from certain points of view an ordinary and a supersaturated solution would, as Dr. Nicol shows, appear to be identical, but a study of the solubility of the salt leads to very different conclusions.

Referring to the nature of solution, Mr. Pickering said that chemists universally recognised two different forms or degrees of chemical combination, atomic and molecular, the latter being in some cases so weak that when examined from certain points of view only we could obtain no evidence of any combination at all; we should do well to consider the strong evidence which a study of minerals, alloys, isomorphous crystals, &c., afford of a form of combination less intimate even than that of our molecular compounds. The true molecules of solids and liquids, he considered, consisted in all probability of a large number of our formula molecules united together, and in the same way the true molecules of a solution would consist of aggregates of a large number of the molecules of the solvent with those of the salt, or of a definite molecular hydrate of the salt, according to circumstances, forming a unit of such complexity and instability that it would probably never exist entirely undissociated, and would therefore be affected in an apparently continuous manner by alterations in the physical conditions under which it existed (see Chemical News, vol. liv., p. 215).

Dr. Armstrong questioned the interpretation which Dr. Nicol had given of the continuous curves by which his observations were graphically expressed. It appeared to be established theoretically that a certain definite electromotive force—over a volt—was required to electrolyse acidulated water; but actually any E.M.F., however small, was found to suffice, the reason being apparently that owing to the presence of dissolved air action took place in a contrary direction: in like manner it was probable that in many cases in which dissociation was observed, if the effect of surfaces, &c., could be eliminated, the changes would be found to take place only suddenly, and would be represented by a broken, not by a continuous, curve. The cases studied by Dr. Nicol were probably of the latter class, and if supersaturation took place gradually—part of the solution becoming supersaturated before even the whole was saturated—the curves representing the change in specific viscosity, &c., would necessarily be continuous. In discussing a problem such as that before the meeting, it was necessary to make a scientific use of the imagination and to consider the phenomena generally.

Dr. Nicol said that Professor Pickering's remarks more than ever convinced him that there was little or no difference in their views. Professor Pickering had abandoned the definite hydrate theory, and now believed in indefinite hydrate-aggregates of one molecule of salt and many hundred molecules of water. Where was the line to be drawn? He (Dr. Nicol) believed at the number of water molecules present in the solution; Professor Pickering stopped short of this, but where? As to the name to be applied to these aggregations, whether they should be called chemical or physical, he thought that according to the present use of the words the latter was the more appropriate. In reply to Professor Armstrong, Dr. Nicol pointed out that in an analogous case Wiedemann had found that the volume curve of hydrated salts exhibited irregularities long before their melting points were reached, and that this pointed to a re-arrangement of the molecules similar to what would occur in supersaturated solutions were the hydrated salt present.

28. "*The Formation of γ-Naphthalenesulphonic Acid by Means of Sulphuric Anhydride, and on γ-Dihydroxynaphthalene.*" By Henry E. Armstrong and W. P. Wynne, B.Sc.

By sulphonating naphthalene by means of sulphuric anhydride, both substances being intimately mixed with sand before admixture, and then vigorously shaken together, the authors have obtained a disulphonic acid which they believe is identical with that prepared by means of $SO_3HCl$ (*Proceedings*, vol. ii., No. 27, p. 230). The sodium salt prepared from the product of the first experiment made at once crystallised in massive transparent diamond-shaped crystals of the oblique system; all attempts to prepare similar crystals from the product of the action of $SO_3HCl$ have beeen unsuccessful, the salt from this source being always obtained in characteristic thin plates; and in a second experiment with $SO_3$ the sodium salt produced crystallised also in plates, distinct, however, in appearance, from those prepared from the $SO_3HCl$ product; and this salt could not be caused to crystallise in the massive forms observed on the first occasion. Nevertheless it can scarcely be doubted that the acids prepared by the two methods are identical, as the sulphochloride rom the $SO_3$ product has the same melting-point (182°) as, and resembles in appearance, that from the $SO_3HCl$ product, and both yield γ-dichloronaphthalene on treatment with $PCl_5$; the products of the action of bromine on the two sodium salts appear to be similar; and they behave alike on fusion with potassium hydroxide.

The dihydroxynaphthalene formed on fusing γ-naphthalenedisulphonic acid with potassium hydroxide would seem to be identical with that prepared by Cléve by Griess's method from the amido-acid formed by reduction of 1 : 4′ nitronaphthalenesulphonic acid. It melts at about 250°; an alkaline solution, on warming, at once assumes a colour like that of a permanganate solution, but the colour rapidly changes to a dirty brown. The authors express the desire to reserve the right of further investigating this dihydroxynaphthalene.

29. "*α-Cyanonaphthalenesulphonic Acid.*" By Henry E. Armstrong and S. Williamson.

It being ascertained that on sulphonating the α haloid-derivatives of naphthalene the products are the 1 : 4 homonucleal sulpho-acid together with a small amount of a heteronucleal isomer, whereas on sulphonating α nitronaphthalene and naphthalene-α-sulphonic acid the 1 : 4′ heteronucleal di-derivative is alone formed, it became desirable to study the behaviour of other α derivatives of naphthalene containing negative radicles. α-Cyanonaphthalene was first sulphonated by means of $SO_3HCl$, but it was found advantageous to use fuming sulphuric acid instead; there appears to be only one sulphonic acid formed. The barium and potassium salts crystallise in different forms according to the conditions, and with different amounts of water; the most characteristic form of the barium salt is a hexhydrated modification $[C_{10}H_6(CN)SO_3]_2Ba.6H_2O$, which crystallises in long, thin, glistening plates; at low temperatures the potassium salt separates in transparent prisms, which probably belong to the oblique system, of the formula $C_{10}H_6(CN)\cdot SO_3K\cdot 3H_2O$. Both salts are dehydrated with difficulty. The sulphochloride,—

$$C_{10}H_6(CN)\cdot SO_2Cl,$$

crystallises from benzene in small glistening prisms. To judge from the result of a preliminary experiment with bromine, it is probable that the cyanosulphonic acid now described is a heteronucleal compound.

30. Addendum to Paper entitled "*An Explanation of the Laws which govern Substitution in the Case of Benzenoid Compounds.*" By Henry E. Armstrong.

In preparing the paper here referred to, having in mind the fact that the "basic" powers of nitrogen become enhanced by introduction of hydrocarbon radicles in place of hydrogen, it appeared to me not improbable that the behaviour of a compound such as dimethylaniline, for example, would not in all cases be strictly in accordance with the para ortho-law; but I did not find any such departure recorded in the indexed literature. I have since become aware, however, that I failed to remember two recent papers, the one by A. Groll (*Ber.*, 1886, 198), the other by E. Nölting (*Ibid.*, 545). According to Groll, dimethylaniline sulphate yields on nitration at a temperature not exceeding 5°, besides the paranitro-derivative, no less than 80 to 85 per cent of *meta*nitrodimethylaniline; diethylaniline behaves similarly. Nölting not only confirms these statements, but adds that ethylaniline sulphate also yields a large proportion meta-derivative; and that on nitrating ethylparatoluidine sulphate, the *meta*nitro-derivative, $NHEt : NO_2 : Me = 1 : 3 : 4$, is exclusively formed; whereas, according to Wurster, the bromodimethylaniline obtained by brominating dimethylaniline dissolved in acetic acid is the *para* modification; and, according to Beilstein and Kuhlberg, paracetoluide yields only the *ortho*nitro-derivative, $NHAc : NO_2 : CH_3 = 1 : 2 : 4$. The facts appear to materially strengthen my argument that the meta-derivatives are formed from an *additive* compound resulting from the association of the reacting molecule with the radicle R' of the parent compound.

In further support of the argument underlying my paper (*Trans.*, 1887, 258), that the formation of an additive compound precedes that of the substitution derivative, I may take the opportunity to point out that on this assumption it is not difficult to understand that, for example, two hydrogen-atoms in ethylic acetoacetate,—

$$Ac{\cdot}CH_2{\cdot}COOEt,$$

are not both immediately displaceable by sodium; probably an additive compound with sodium ethoxide is first formed, which becomes resolved into alcohol and acetosodacetate,—

$$Ac{\cdot}CH_2\,CO_2Et + NaOEt = Ac{\cdot}CH_2{\cdot}(CO_2Et{\cdot}ONaEt) = Ac{\cdot}CHNa{\cdot}CO_2Et + EtOH;$$

owing to the influence which the sodium exercises on the contiguous $CO_2Et$ group, this is no longer capable of uniting with sodium ethoxide, and only recovers the power of so doing on displacement of the sodium by a hydrocarbon radicle.

31. "*The Transformation of Citric Acid into Pyridine-derivatives, and on the Constitution of Pyridine.*" By S. Ruhemann, Ph.D., Jacksonian Demonstrator in the University of Cambridge.

Hofmann and Behrmann have shown that citramide is converted by heating with sulphuric acid into citrazinic acid, the dihydroxypyridinecarboxylic acid, in which both hydroxyls are in ortho-positions to the nitrogen-atom, the carboxyl being in the para-position. The author finds that the formation of the pyridine-derivative takes place even at ordinary temperatures if ethylic aceto-citrate be mixed with strong aqueous ammonia, and the mixture allowed to stand several days; dilute chlorhydric acid then precipitates citrazinamide. The production of a pyridine-derivative in this manner is a strong argument, he thinks, in favour of Riedel's contention that the nitrogen-atom in pyridine is in connexion with the carbon-atom, which relatively to it is in the para-position; and in further support of this view he states that no condensation takes place if methylamine be substituted for ammonia, there being in this case no available hydrogen-atom associated with the nitrogen-atom to separate with the hydroxyl, and thus permit of the union of the nitrogen-atom with the para-carbon-atom. Incidentally it is mentioned as an indication of the mobility of the acetyl-group that if ethylic aceto-citrate be treated with phenyl hydrazine, the acetyl-derivative if the latter is formed; ethylic acetomalate and diacetotartrate behave similarly.

32. "*Silver containing Bismuth.*" By William Gowland, A.R.S.M., Chemist and Assayer of the Imperial Mint, Osaka, Japan, and Yoshimasa Koga, Assistant Assayer.

An account is given of assays and metallurgical experiments made with the object of determining the effects produced by the presence of small quantities of bismuth on the ductility of silver, and on the uniformity of composition of silver bullion when in ingots of the form and size ordinarily met with in commerce. It is found: *α*. That when silver is obtained from copper containing bismuth by the liquation process with subsequent cupellation of the argentiferous lead, it contains part of the bismuth which was present in the copper; *β*. That this silver is brittle even when containing bismuth in but small amounts; *γ*. That ingots of such silver are not uniform in composition throughout their mass, the parts which have solidified last being richer in silver than the others; *δ*. That when coinage bars of 900° millesimal fineness are prepared from it, they cannot be rolled without special treatment, and even then are hard and unsuitable for mintage.

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The Anniversary Meeting will take place on March 30, at 8 p.m.

At the next Ordinary Meeting, on April 7, the following paper will be read:—

"Researches on the Constitution of Azo- and Diazo-derivatives. Diazoamido-compounds (Part II.)," by R. Meldola, F.R.S., and F. W. Streatfeild.

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## PHYSICAL SOCIETY.

*March 12th*, 1887.

Prof. G. Carey Foster, Vice-President, in the Chair.

Mr. Shelford Bidwell described some experiments which seem to show that the electrical resistance of suspended copper and iron wires alters with the direction of the testing current. The apparatus used consisted of a metre bridge with coils of 100 ohms in the gaps adjoining the standard wire, the other two arms being two suspended wires united at the top, to which point one terminal of the galvanometer was joined. A commutator placed in the battery circuit served to reverse the testing current.

When a wire is suspended vertically the stress increases from below upwards, and the author believes the observed effects due to the absorption of heat by the current as it passes from a stretched towards an unstretched part of a copper wire, and the evolution of heat when it passes from an unstretched towards a stretched part. As the apparatus was arranged the current passed up one wire and down the other, heating the one and cooling the other, thus disturbing the position of balance. If iron wires are used the heating and cooling effects are reversed.

Prof. S. P. Thompson suggested loading the wires at different points, in order to vary the stress without using such long wires; and Mr. C. V. Boys thought that still shorter wires could be used, by joining the ends to a revolving spindle and stretching them by centrifugal force.

"*On a Lecture Experiment in Self-Induction.*" By Mr. Shelford Bidwell.

A telephone is placed in series with the secondary coil of an induction-coil, and another coil whose self-induction can be varied by inserting a core of iron wires or another coil, or both. The effect of introducing the iron core is very marked, reducing the sound enormously. If a coil of wire containing an iron core be inserted, the effect of short-circuiting the coil increases the sound in the telephone.

The same author also described and showed an experiment due to Dr. Fleming, in which a disc of copper

inclined at an angle of 45° to the axis of a coil of wire, and suspended bifilarly, is deflected by passing an undulatory current round the coil.

In explanation of the former experiment Dr. FLEMING wrote down the formula for the effective resistance and self-induction of a circuit near another closed circuit, which show that the former is greater and the latter less for undulatory than for steady currents. He had not arrived at any satisfactory explanation of the deflection of the copper disc.

Prof. AYRTON exhibited a tuning-fork worked electrically, in which the pitch could be varied by altering the self-induction of the circuit, or by varying the position of the make and-break screw.

Mr. C. V. BOYS referred to his experiments, published in 1884, on the impulse given to metal discs suspended in a magnetic field, whose strength is suddenly changed, as being of a similar character to that described by Mr. Bidwell, and suggested the use of aluminium instead of copper in future experiments, owing to its conductivity for the same weight being greater.

Prof. THOMPSON said he had recently used a similar apparatus to that described by Mr. Bidwell as an illustration of the effect of self-induction, and pointed out the uses of self- and mutual-induction in multiplex telegraphy and telephony.

As an explanation of the deflection of the copper disc by alternating currents, Prof. FOSTER thought it possibly due to its initial position being that of maximum sensibility, and therefore each impulse had less effect then the preceding one.

Mr. W. M. MORDEY mentioned a simple arrangement for varying self-induction used by Mr. Ferranti to control the power of incandescent lamps worked by alternating currents; and Prof. AYRTON described a closed magnetic circuit of great self-induction, used to protect voltmeters on the telpher line at Glynde from disastrous inductive effects produced by breaking the locomotive circuit.

Referring to tuning-forks, Mr. BOSANQUET thought some self-induction was necessary in order that the current should act to the best advantage in attracting the prongs at the proper instant.

Further remarks were made by Mr. BOYS and Prof. PERRY.

"*On a Lecture Experiment to show that Capacity varies Inversely as the Thickness of the Dielectric.*" By Profs. W. E. AYRTON and JOHN PERRY.

The authors consider it easy for students to see that, other things remaining constant, capacity is proportional to area. Taking this as proved, a condenser is arranged such that the area, A, of the insulated inner coating varies as the thickness, $t$, of the dielectric, and the potential difference between the coatings is found by experiment to be constant. Then, since—

$$\text{Capacity} = \frac{\text{Quantity}}{\text{Potential}},$$

and both the latter being constant, therefore the capacity of the condenser is constant. But by the construction of the apparatus $\frac{A}{t}$ is constant, and it is assumed that capacity varies as A; therefore capacity must vary inversely as $t$.

"*Note on Magnetic Resistance.*" By the same Authors.

Two iron rings, about 6 inches diameter, made from the best Swedish iron, about ½-inch diameter, were wound with insulated wire in two halves, so that a current could be sent round either or both halves, and the resulting induction measured by the throw of a ballistic galvanometer placed in series with a few convolutions of wire wound round the outside of the main winding. One of the rings was continuous, and the other had a small air-space of about 0·8 m.m. in a plane perpendicular to that of the ring and passing through its axis, as if the ring had been cut by a saw. The primary object of the experiments—which were made by Messrs, Aldworth, Dykes, Lamb, Robertson, and Zingler, of the Central Institution—was to determine whether there was any appreciable "surface magnetic resistance" The results do not show any such resistance; and the relative resistance of air and iron, as calculated from the unsaturated parts, are about as 1200 to 1, a number agreeing fairly well with those obtained by other experimenters. From this the authors conclude that for small distances magnetic resistance of air is proportional to length. When the magnetising current was passed round the one-half of the divided ring on which the test coil was wound, a greater induction could be obtained than by any other way of magnetising, and this the authors do not attempt to explain.

Mr. BOSANQUET said he had always found greater inductions obtainable in the middle of bar electro-magnets or open magnetic circuits than could be produced in closed magnetic circuits, and thought the above observations confirmed his own results.

A discussion followed, in which Mr. C. V Boys, Mr. W. M. MORDEY, Mr. BOSANQUET, and Prof. PERRY took part.

On account of the late hour the reading of a "Note on Dynamo Machines and Motors," by Profs. Ayrton and Perry, was postponed till the next meeting

## NOTICES OF BOOKS.

*Address to the Agricultural and Horticultural Association, Limited.* By ED. O. GREENING. 1887.

IN commenting on some very desponding remarks on the subject of British Agriculture, recently made by Mr. C. S. Read, in which he declares that, on scanning the whole social horizon, he can see no hope from any quarter, Mr. Greening boldly states that things are not so bad as some people would have it believed; scientific men may have blundered in their advice to farmers, engineers have sometimes made uneconomical machines, but, he asks the British landowners and farmers:—Have you really exhausted all the resources of your knowledge, your experience, your powers? In reply, Mr. Greening, in the first article of the accompanying pamphlet, hopes he has clearly shown how members of this Association, now entering on its twentieth year, can obtain exactly the fertilisers required to grow the greatest crops at the smallest cost, and with absolute immunity from danger of exhausting the soil.

The title selected for the above-mentioned article, which accompanies this address, is "Does it Pay to Use Complete Manures?" This question is in reality a very simple one, though it is generally complicated by other questions which have nothing to do with it; it can, however, be easily solved by answering the following:—

1st. What is the cost of the manure and it application?
2nd. What is the increased value of the crop?

Last year one of the members of the Association, Mr. Bellairs, made some very careful experiments on manuring potatoes; the soil was poor, and moderately light, frequent showers favoured the dissolving of the artificial manures, and during the first two months the superior growth of one plant showed the advantage of manuring *up the furrows* instead of on the surface, as is so frequently advocated in these days. The weights of the manures applied and the potatoes yielded are given, and show a balance in favour of artificial manure of £12 per acre. The conclusions from these experiments are:—

1. That there is a large profit on the use of complete potato manure of scientific proportions.

2. That in these experiments the highest result (with one exception) were obtained with the use of No. 6 manure (as supplied by the Association) mixed with salt, gypsum, and ashes in the proportions stated.

3. The exception was in favour of good dung ploughed in, with a top-dressing of No. 6, but as the cost and quality of the dung was unknown, the comparative profit or loss of this treatment cannot be accurately judged.

4. Neither sulphate of potash alone, or gypsum and salt, produced such favourable results as the complete manure No. 6, though the combination of the two latter was distinctly advantageous.

5. Better results were obtained by applying the manure as a top-dressing when the potatoes were planted, than at a later period.

6. The best results of all were obtained by sowing the No. 6 with salt and gypsum up the furrows and not on the top.

A number of letters are quoted from different users of these manures, all testifying to their value; one gentlemen states that "one drill, manured twice by mistake, yielded, at an extra cost of 2s. 4d., 3 cwt. more potatoes than the adjoining drill, showing that, even at the present low values, there would be more profit by doubling the manure than by using the amount prescribed. From these und other results here given, it is clear that high manuring with complete manures pays better than stinting the outlay. An average of thirty years continuous wheat-growing on the same land shows that unsuitable manure costing 40s. per acre is almost money thrown away; that nitrate of soda worth £2 15s. per acre gives an extra profit of £3 10s., and that a complete manure costing £4 10s. produces an increased profit of £7 17s. 6d. per acre. We further find that, in a bad year, complete manure pays an extra profit of £2 10s. per acre, on an average of years £3 7s. 6d., and in a good year it will pay £4 10s., calculating the wheat at its very lowest value. The moral of this is, as Mr. Greening says, that instead of ceasing to use manure in good seasons and relying upon the weather, a wise agriculturist should double his outlay at such a time, and double his gains while circumstances give him the golden opportunity.

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*The Graphical Representation of the Relation between Valence and Atomic Weight.* By C. J. Reed. 1886.

In these days, when the relations between matter and matter, and even the primal composition thereof, is attracting considerable attention from scientific men of all classes, any fresh information or ideas bearing in any way on the subject are sure to be carefully considered.

Mr. Reed has approached the question from a mathematical point of view, and he starts with the three following hypotheses, which were first announced, though in a different form, by Mr. O. C. Johnson in the Chemical News, vol. xlii., p. 51.

Hypoth. I. *The valence of an atom is its capacity for electro-polarity.*

Hypoth. II. *The polarity of an integrant molecule is always zero.*

Hypoth. III. *Positive and negative changes of polarity are always contemporaneous and equal.*

All the atoms in a molecule are to be considered as polarised, one-half the atoms (measured in *valence*, not in numbers) positively, and the other half negatively; an atom is *neutralised* when it is united with one or more atoms having the same degree of polarity but of opposite sign, neutralisation meaning opposition, and not that the polarity is destroyed; thus, two atoms united into a molecule may be compared to two permanent magnets united by their opposite poles, forming a molecule which would present no external polarity. Mr. Reed gives a very clear illustration of this conception, but unfortunately it cannot be followed without having reference to the accompanying diagrams.

In Part II. are given the atomic weights and observed valence of the elements, and the principal compounds in which those valencies occur. In compounds which cannot be electrolysed the more basic elements are considered electro-positive and the more acidic electro-negative.

Part III. deals with the graphical representation of the relations detailed in Part II., but in the absence of a diagram we cannot make this perfectly clear; the manner of plotting is, however, as follows:—Two straight lines meet at right angles at zero, the vertical line representing valence ×10 and extending to 40 below zero, and the horizontal line representing atomic weight, a point is located on the plane for the maximum, minimum, and characteristic valence of each element, and nearly all these points are found to lie on a double series of parallel lines, the successive pairs of which are separated by equal distances, the deviations from these positions is so slight as to be barely noticeable on the scale used; after considering this diagram and pointing out some periodic and recurrent combinations, Mr. Reed concludes that "*saturation-valence is an equicrescent rotatory function of atomic weight*," and in order to represent this idea graphically he locates the points on the surface of a cylinder instead of on a plane. He next points out that he has considerable grounds on which to base the conclusion just quoted, which he claims can hardly be a coincidence from the fact that it unites not less than fifty chemical elements by so simple a relation between valence and atomic weight; whether this conclusion is or is not the expression of a natural law he leaves for others to decide after mature consideration, but we must admit that on first sight there seems to be very reasonable grounds for the assumption.

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# CORRESPONDENCE.

## METHOD OF PREPARING GRAPHITOIDAL CARBON FOR ELECTRICAL INCANDESCENCE.

*To the Editor of the Chemical News.*

Sir,—Under this heading in your last issue Mr. H. N. Warren describes a method for preparing carbon filaments for incandescence lamps by the passage of an electric spark through coal-gas, and the consequent decomposition of the gas with deposition of carbon upon one of the electrodes. The method, however, is not novel, for in November, 1882, it was patented (British Patent No. 5373 of 1882) by myself in conjunction with Messrs. J. M. Boullon and Isaac Probert; and three years later was apparently re-patented by Mr. Alexander Bernstein (British Patent No. 13,036 of 1885).

The fact that a deposit of carbon can be obtained upon one of the electrodes during the electrolysis of a carbonaceous gas is of course much older than either of these patents. Everyone who has used a Hofmann's tube for showing the volumetric composition of marsh-gas is familiar with the partial or complete bridging over of the spark space which occurs during the progress of the experiment.—I am, &c.,

Alfred W. Soward.

March 21, 1887.

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## RELATION OF THE CHEMICAL CONSTITUTION OF INORGANIC COMPOUNDS TO THEIR PHYSIOLOGICAL ACTION.

*To the Editor of the Chemical News.*

Sir,—In the Chemical News (vol. lv., p. 110) is an article on this subject, stated to be a report of a paper I read before the University College Physical and Chemical Society. The paper I read before the Society was a different thing altogether. Its object was to point out some of the defects in our methods of scientific teaching, particularly as regards the neglect of the historical development of the different sciences, and also to emphasize the advantages of such societies as the one I was addressing, from their tendency to counteract the evils

resulting from the too specialised pursuit of any one science. The article published in the Chemical News contained merely some extracts from a paper read before the Chemical Society in December, and which were introduced into my address partly from some historical reminiscences connected with my earlier experiments which were made in the same locality just half a century ago; but principally as, in reviewing the criticisms that had been made on my work, I had an opportunity of pointing out some striking examples of the evils of a too specialised pursuit of any one branch of science, which evils it was the object of the Society I was addressing to counteract.

The paper as published in the Chemical News is very analogous to the play of "Hamlet" with Hamlet left out. As I had no opportunity of seeing a proof I would correct two errors which occur in the paper: one in relation to the relative quantities of the reagents, page 111, where the quantity for Mg should be 0·080 instead of 0·030; and another, on the same page, where Schmeidebeg should be substituted for Schmerdehery.—I am, &c.,

James Blake.

[Want of space prevented our publishing the paper in full; we gave, therefore, only the chemical part.—*Ed.* C. N.]

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 9, February 28, 1887.

**Phosphorescence of Calcium Sulphide.**—Edmond Becquerel.—Inserted in full.

**Red Fluorescence of Alumina.**—Lecoq de Boisbaudran.—It has been already stated that alumina, after strong ignition, though it gives a bluish fluorescence in a vacuum, gives a red colouration in the phosphoroscope. The writer, however, thinks that this observation does not subvent his hypothesis of the presence of chrome as necessary for the production of the red fluorescence of alumina.

**Coefficients of Chemical Affinity.**—P. Chroustchoff and A. Martinoff.—Berthollet, as it is well known, announced the following rule: the chemical actions of bodies are simply proportional to the numbers of their equivalents present. Subsequent researches have led several chemists to put forward much more complicated laws to which the phenomena of transformation may be subject. Berthollet's rule has been re-modelled by the introduction of certain coefficients, called coefficients of affinity, which are alleged to give the measure of the affinity peculiar to different bodies. The researches of M. Berthelot have, however, proved that one of the forms of these coefficients of affinity, that known as the *avidity* of acids for bases, does not possess the character of a true constant. These conclusions have led the authors to undertake the experimental revision of one of the methods which have been thought applicable for determining these coefficients. From the results thus obtained they infer that the primitive composition of mixed precipitates formed by a mixture of salts in equal numbers of equivalents approaches a symmetrical distribution with about 50 per cent of each of the insoluble salts. The phenomenon of precipitation is constituted in the like cases by the superposition of two distinct phases, *i.e.*, a perfectly mechanical distribution according to the initial chances of meeting of the three bodies mixed, and a secondary transformation (simultaneous or consecutive) of the precipitates when once formed by the surrounding liquids; this secondary reaction being produced with a variable rapidity. Neither the initial composition nor the final composition (stable equilibrium) of the precipitates can give the coefficients of chemical affinity. Hence constants characteristic of affinity cannot be elaborated by the method of simultaneous precipitation.

**Characters of Debilitation experienced by Diastase if Submitted to the Action of Heat.**—E. Bourquelot.—Weakened diastase, even if used in excess, has lost the power of carrying the decomposition of starch to its ultimate limit. Yet this same diastase effects the first phases of the reaction as rapidly as natural diastase. It is suggested as possible that there may exist in natural diastase two or more soluble ferments in a state of mixture, and that an elevation of temperature destroys them successively.

**The Earths of Cerite.**—Eug. Demarçay.—The author has formerly shown that the absorption band $\lambda = 417$ attributed to samarium does not belong to the same body as that which furnishes the band $\lambda = 400\,7$. He has since pursued the fractionations, and has arrived at results which he now lays before the Academy. As regards samarium he confirms his former results, and adds that the band $\lambda = 417$ does not belong to the body which furnishes the blue bands $\lambda = 480$, $\lambda = 463$; concerning the common or distinct origin of the three bands $\lambda = 400$—$480$—$463$. Among the products of these fractionations there are earths very rich in praseodyme, and others in which it is absent. The fractions comprised between pure praseodyme and neodyme present the band $\lambda = 469$ equal in strength to $\lambda = 444$ (the latter attributed by Auer von Welsbach to praseodyme), but with an intensity greater than that which it presents in earths consisting of almost pure praseodyme. Hence this band would seem to represent a distinct body. The author has not observed with certainty a corresponding variation in the other bands of praseodyme, nor in those of neodyme. The bands $\lambda = 476$ and $\lambda = 462$ seemed to vary simultaneously. The methods used for these fractionations are precipitation with dilute ammonia, oxalic acid in very acid solutions, crystallisation of the ammoniacal nitrates, and the precipitation of the sulphates and double potassium sulphates by alcohol.

**On Zinc Ferrite; The Artificial Production of Franklinite.**—Alex. Gorgen.—The author gives methods for preparing zinc ferrite, and compares this artificial product with the natural mineral franklinite.

**Incompatibility of Nitrates and Superphosphates.**—A. Andouard.—A mixture of mineral superphosphate and soda salpetre contained, when prepared, at the end of May, 1886, 6 per cent of nitric nitrogen. By July 12 it had gradually fallen to 3·78 per cent. Other mixtures, both on the large and the small scale, gave corresponding results. This loss was observed with bone superphosphates as well as with that from phosphatic minerals. The presence of sulphate of ammonia and, apparently, of nitrogenous organic matter, does not retard this waste. The free phosphoric, sulphuric, and hydrofluoric acids present displace the acid of the nitrate, which escapes either as such or, after being gradually reduced by the oxidisable substances present. Hence it is an error to associate nitrates with superphosphates in manures. Decomposition can be retarded only by employing the nitrate in coarse fragments, which of course interferes with its uniform distribution in the soil.

**Cause of the Changes observed in Blood in Contact with Air, Oxygen, and Carbonic Acid.**—A. Béchamp.—The changes with take place in blood, whether in contact with oxygen or carbonic acid, are effected only by means of the activity of the microzymas present.

**The Deposits of Tin from a Geological Point of View.**—M. Reilly.—The author shows that the chief deposits of tin lie on or near a great circle which he calls the axis of Sumatra.

*Moniteur Scientifique, Quesneville.*
Series 4, Vol. i., (Part First), February, 1887.

History of Californian Borax.—A. Robottom.—From the Chemical News.

Studies on Mordanting Wool.—MM. Liechti and Schwitzer.—Translated here from the *Journal of the Society of Chemical Industry*.

Determination of Nitrogen according to Kjeldahl.—After giving the opinions of a number of chemists the author concludes by saying that Kjeldahl's method is likely to do good service for the analysis of manures, articles of food, forages, and the majority of organic nitrogenous substances. It is not applicable to the amines with aromatic nuclei. The results are also uncertain if the substance contains much nitrate. It is therefore applicable for all cases where the process of Will and Varrentrap is commonly used, and it has, in comparison with the latter, the advantage of being quicker, easier, and more economical.

A Laboratory Accident.—E. Divers.—From the Chemical News.

Determination of Empyreumatic Oils in Spirits.—A. Stützer and C. Reitmar.—The authors' method is based upon the influence of ethereal oils upon the height to which water and alcohol ascend in capillary tubes.

Phenazine and its Derivatives.—From the *Berichte der Deutsch. Chem. Gesellschaft.*

Communications on Germanium.—Clemens Winkler.—Already noticed.

Certain Simple Bodies, probably New.—Al. Pringle.—From the Chemical News.

Synthesis of Aromatic Bodies, effected by Means of Aluminium Chloride.—This extensive memoir bears no author's name. The results may be summarised as follows:—The dyssymmetric dibenzyle and diphenylethylene resulting from the reaction of the isomeric dibromethylenes in presence of aluminium chloride are formed without an intermolecular displacement of the atoms taking place, and they have consequently the same constitution as the dibromethylenes from which they are derived. The synthesis of anthracene effected by the aid of acetylene tetrabromide, of benzine, and of aluminium chloride renders the hypothesis probable that in anthracene the two atoms of carbon occupying the *meso*-position are connected together. Dimethylanthracene, melting at 225°, being obtainable by the reaction of tetr -brom anthracene upon benzine in presence of aluminium chloride, we must admit that there are two methyl groups fixed upon the benzinic nuclei. Aluminium chloride possesses not merely the power of splitting the lateral chains of the methylbenzines and ethylbenzines, but it also determines the removal of the split chains from one molecule of the hydrocarbon to another. In this migration the same methyl benzines may be formed by the addition of the methyl-groups to the less methylated benzines, which are formed by the loss of these groups in the more methylated benzines. Tetraphenylmethane obtained synthetically by the reaction of β-styrolene bromide, stilbene bromide, or tolane bromide upon benzine in presence of aluminium chloride is identical crystallographically with the tetraphenylethane obtained from succinic acid and benzhydrol, chloride of benzhydrol, benzophenone, β benzpinacoline, and tetraphenylethylene. Hitherto, in consequence, we know only one of the two isomeric tetraphenylethanes, which are theo etically possible. The separation of bromine in the tetra-brom-ethanes and vinyle tribromide, treated with aluminium chloride in presence of benzol, is proved indirectly by the presence of benzine bromide among the products of the reaction. By the reaction of ethylidine bromide, ethylidine chloride, and vinyle bromide upon benzine in presence of aluminium chloride, we obtain synthetically, along with dissymmetric ethylbenzine and diphenylethane meso-dimethyl-anthracene hydrate. Ethylidene chloride, toluene, and aluminium chloride yield, along with dissymmetric ethyl-toluene and ditolylethane, hydrated tetra-methyl-anthracene.

Academy of Medicine: Salicylic Acid.—After a prolonged discussion it was decided that even small doses of salicylic acid and its derivatives, if often repeated, may occasion serious derangements of health in elderly persons, and in all in whom the digestive and the urinary organs are not in perfect order. Hence the addition of salicylic acid and its derivatives to articles of food and drink cannot be authorised.

Industrial Society of Mulhouse.—Chemical Committee, November 10, 1886.—A sealed paper which had been deposited by M. Weingaertner was read. It relates to the preparation of phenyl-methoxyquinizine.

H. Kœchlin mentioned that in dyeing turkey reds he has been able to dispense for the last ten years with the clearing process with soap-lye under pressure, using merely water or steam, and suppressing the sulpholeic preparations which precede this process. He adds to the dye beck stannic acid, obtained by precipitating the nitromuriate of tin with sodium carbonate.

Session of December 8, 1886.

M. Oscar Scheurer gave an account of his experiments on the fixation of iron mordants in presence of phosphorous acid and of a copper salt.

Contributions to the Chemical Analysis of Iron, Steel, and Cast-Iron.—An account of the proceedings at a meeting of Russian iron-masters. As regards the determination of carbon, the method of Eggertz is considered as deffcient in accuracy.

The Quantity of Cinchonidine contained in the Quinine Sulphate of Commerce.—O. Hess.—An acrimonious reply to a paper by M. de Vrij.

Detection of Wheat-Flour in Chocolate.—Dr. G. Pennetier.—A microscopic method.

## MEETINGS FOR THE WEEK.

Monday, 28th.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "Machines for Testing Materials, especially Iron and Steel," Prof. W. C. Unwin, F.R.S.
Tuesday, 29th.—Institution of Civil Engineers, 8.
—— Royal Institution, 3. "Function of Respiration, by Prof. Arthur Gamgee, F.R.S.
—— Society of Arts, 8. "Colonial Wines," by Richard Bannister.
Wednesday, 30th.—Society of Arts, 8. "Electric Locomotion," by A. Reckenzaun.
—— Chemical, 8. (Anniversary).
Thursday, 31st.—Royal, 4 30.
—— Royal Institution, 3. "The Science of Thought, by Prof. F. Max Müller, M.A., LL.D.
Friday, April 1st.—Royal Institution, 9. "Light as an Analytic Agent," by Professor Dewar, M.A., F.R.S.
—— Geologists' Association 8.
Saturday, 2nd.—Royal Institution, 3. "Sound," by the Right Hon. Lord Rayleigh.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Hard Water and Stone.—Since my last communication I have been informed by a medical man that stone is most prevalent in places of least rainfall, and *vice versa*, *e.g.*, Norfolk and the Lake District. In India stone is of common occurrence.—Sm.

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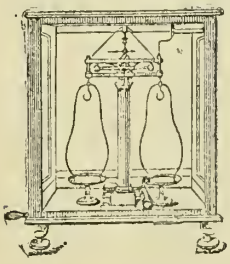

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ST. PAUL'S SCHOOL.—An Examination for filling up about Four Vacancies on the Foundation will be held on the 21st April, 1887.—For information apply to Mr. S. BEWSHER, Bursar, St. Paul's School, West Kensington.

THE CHEMICAL NEWS.

VOL. LV. No. 1427.

ON THE

# BEHAVIOUR OF ALKALINE SOLUTIONS OF PHENOL-PHTHALEIN IN THE PRESENCE OF ALCOHOL.

By HARRY NAPIER DRAPER, F.C.S., and CARTER DRAPER.

(Concluded from p. 134.)

## PART II.—PHENOL-PHTHALEIN WITH ALCOHOL, AND POTASH OR SODA.

As the results obtained with ammonia appeared of sufficient interest to render desirable an examination of the behaviour of phenol-phthalein with potash and soda in the presence of alcohol, a number of preliminary and parallel observations were made, which demonstrated that both bases present, though in different degree, the same phenomena. Potash was selected for the enquiry, and it is to be understood that the experiments cited in the following notes were made with potassium hydrate.

The standard solution of phenol-phthalein employed was the same as that used in the ammonia experiments, and the potash and soda solutions contained respectively 1 grm. of KOH and of NaOH in 100 c.c. of absolute alcohol.

One c.c. of the phenol-phthalein solution and 1 c.c. of the potash solution were mixed with 20 c.c. of alcohol in a beaker. Such a solution containing ammonia instead of potash would have become instantly colourless, or rather would not have become coloured at all, but this remained deeply red. The colour, however, gradually faded, and after a short time the liquid was colourless. To determine the time occupied in bringing about the decolouration several experiments were made, and the mean result of these showed it to be, at 15° C., forty-five minutes.

It was at first assumed that the reaction here was analogous to that with ammonia,—that is, that the anhydrous phenol-phthalein salt of potassium being probably colourless, any water present in either the phenol compound or the potash was gradually dissociated by the action of the alcohol.

That, indeed, either the anhydrous potassium salt of phenol-phthalein is colourless, or that in the absence of water no combination takes place, may be demonstrated by impregnating white bibulous paper with a dilute solution of potassium hydrate, and then, after careful drying, moistening it with alcoholic phenol-phthalein. The paper thus prepared remains practically colourless. For obvious reasons this experiment requires careful manipulation, but may be more easily made if a watery solution of the carbonate be substituted for the alcoholic solution of the hydrate. In either case the faintly tinted paper becomes, upon moistening with water, intensely coloured.

But that this assumption was not tenable, soon became evident. In the first place, addition of water to the decolourised alcoholic solution did not restore the colour. Secondly, it was not probable that the small quantity of water present could—in the presence of so large an excess of alcohol—effect so deep a colouration of the liquid. Thirdly, a further addition of alcoholic solution of potash to the decolourised liquid restored its colour.

The next step taken was the substitution of water for the alcohol. A mixture consisting of 1 c.c. phenol-phthalein solution and 1 c.c. of the potash solution, with 20 c.c. of water exposed in an open beaker, had not become colourless in three days,* and in this case, also, the colour was restored by further addition of potash. There was thus indicated a marked difference between the behaviour of alcohol and that of water, which led us to suppose that if the quantity of alcohol added were increased, the decolouration might be more rapidly effected; but many experiments with varying quantities of alcohol afforded no support to this view.

When a phenol-phthalein-potash-alcohol solution was contained in a quite filled and closed flask the colour remained permanent. This pointed to atmospheric action as the cause of the colour destruction. To ascertain if it were due to oxidation the following experiments were made:—

The solution was exposed for three days in an atmosphere of pure oxygen without undergoing any loss of colour.

To 20 c.c. of the coloured liquid there were added at intervals 32 c.c. neutral hydrogen peroxide of 10 per cent. After three days it had become nearly colourless.

To a trace of potassium carbonate dissolved in water excess of alcohol was added, and then phenol-phthalein. The colour of this solution was at once destroyed by hydrogen peroxide.

Ethereal solution of hydrogen peroxide acted in the same way, but more rapidly.

The introduction into solutions decolourised by hydrogen peroxide of a copper-zinc couple restored the colour after some hours, but the action of a palladium-hydrogen couple was without effect. Dry and carefully purified hydrogen passed for some time through the liquid was equally ineffective.* It was thus evident that the colour restoration brought about by the copper-zinc couple was due to the formation of zinc oxide, which we have found to be, when recently precipitated, sufficiently soluble in water to give a marked colour reaction with phenol-phthalein.

When the solution decolourised by exposure to air is boiled for a few minutes in an open tube its colour returns, and when again cooled it becomes colourless.

In a sealed tube no restoration of the colour takes place, even after prolonged heating at 100°. If again an open tube, in which, after boiling, the liquid has become coloured, be at once closed, the latter remains coloured for a short time, but afterwards becomes colourless.

It being now sufficiently probable that the decolouration was due to atmospheric carbonic acid, the enquiry took this direction.

In an atmosphere of hydrogen, the red solution after forty-eight hours still remained red.

In air, which had been carefully freed from carbonic acid, there was in twenty-four hours no decolouration.

When dry air was rapidly aspirated through the liquid it became decolourised in thirteen minutes; when the air was passed through potash tubes, and the same rate of aspiration employed, seventy-five minutes were required. From other experiments it was found that the time required for decolouration was directly as the rate of aspiration, indicating of course greater or less absorption of carbonic acid by the interposed potassium hydrate.

A few drops of water saturated with carbonic acid produced immediate decolouration of the liquid.

If 1 c.c. each of the solutions of phenol-phthalein and potassium hydrate be mixed with 20 c.c. of alcohol, through which a current of carbonic acid has been passed, the colour is instantly destroyed; but alcohol which has been previously boiled may, on the contrary, be added in large quantity without causing decolouration.

In the experiments with ammonia it has been noted that the quantity of unboiled alcohol required to effect decolouration was notably less than of alcohol which had been boiled; but in the case of the fixed alkalies no dissociating action seems to be exerted by alcohol, and the loss of colour appears to be wholly due to the absorption of carbonic acid by the alcoholic solution.

* In another experiment eleven days were required to effect decolouration.

* The destruction of the colour by neutral hydrogen peroxide is somewhat ambiguous, but we have not pursued the reaction further.

It has been already shown that watery solutions require for decolouration a very much longer time than those in alcohol. That decolouration in an aqueous solution should occur at all, can indeed only he due to the ultimate formation of an alkaline bicarbonate, because if the action of the absorbed carbonic acid stopped short at the formation of carbonate the colour of the solution would remain unchanged.

The greater rapidity of decolouration of an alcoholic solution is due to two causes: firstly, to the larger solubility of carbonic acid in alcohol than in water. According to Fehling*—

| | | | | |
|---|---|---|---|---|
| 1 vol. water | at 0° C. | dissolves | 1·79 | vols. $CO_2$. |
| 1 ,, ,, | ,, 14° ,, | ,, | 1·03 | ,, |
| 1 ,, alcohol | ,, 0° ,, | ,, | 4·32 | ,, |
| 1 ,, ,, | ,, 18° ,, | ,, | 3·04 | ,, |

Secondly, to the complete insolubility of potassium carbonate in cold alcohol, for such weak solutions as we have employed become very rapidly carbonated when freely exposed to the atmosphere.

So that the absorption of carbonic acid to the extent of formation of a bicarbonate (a necessary condition for the decolouration of an aqueous solution) is not necessary where alcohol replaces the water. Indeed if the proportion of potassium hydrate be about five times greater than that employed in the above experiments, the solution, which in this case of course requires a much longer time for decolouration, deposits a precipitate of pink-tinted carbonate in a perfectly colourless liquid. Finally, the carbonate itself becomes colourless. If, however, before this decolouration takes place, a portion of the coloured carbonate be removed from the liquid and dried, it loses its colour. That the supernatant liquid in this case contains potassium bicarbonate, and not carbonate, may be demonstrated by a careful application of the mercuric chloride test.

Potassium bicarbonate is, according to Gmelin,† soluble in 1200 parts of alcohol, and it is upon this fact that the phenomena observed on heating the decolourised alkaline phenol-phthalein alcoholic solution depend. In a sealed tube this may be heated without change, but on boiling in an open tube it loses carbonic acid, and in a few minutes the colour is restored. If the solution be now cooled the colour disappears, and that this is due to reabsorption of carbonic acid is proved by the fact that if the cooled tube be again sealed the colour is no longer restored on heating to 100°. But if, on the contrary, the tube be sealed as rapidly as possible while the contained liquid is still hot and coloured, the latter becomes, as before, colourless on cooling, but *the colour is at once restored when it is again heated.*

The explanation of this reaction is due to the—we believe—hitherto unobserved fact that potassium carbonate, which is quite insoluble in cold alcohol, is soluble in alcohol at 100°. The bicarbonate formed by absorption of carbonic acid from the atmosphere by an alcoholic solution of an alkaline hydrate becomes monocarbonate on heating, but this, being insoluble in cold alcohol, is unable to form a coloured compound with the phenol-phthalein until the liquid in which it exists being heated it dissolves, and affords another most striking illustration of the axiom "Corpora non agunt nisi soluta."

We have verified these conclusions by direct experiment with potassium carbonate and bicarbonate.

We desire also to note that the insolubility of potassium carbonate in cold, and its solubility in hot, alcohol, may be equally demonstrated if the colouring-matter employed be turmeric instead of phenol-phthalein; a solution of curcumine in absolute alcohol, in which a trace of pure and dry potassium carbonate is present, remaining in a sealed tube without change of tint, to become at once deeply reddened on heating to 100°.

* *Handworterbuch*, Band iii., S. 1058.
† Vol. iii., p. 25.

## ON A FUNDAMENTAL LAW OF THERMO-CHEMISTRY.*

By CLARENCE A. SEYLER.

ONE of the most striking features of modern chemico-physical results is the demonstration of properties in a compound which are the sum of those of their components. This indeed is a necessity for the atomic theory, which supposes that bodies react in terms of units whose integrity remains inviolate throughout all changes. Up till recently, however, it was thought that mass was the only property of which this is true. Modern researches, however, have revealed it not only in the case of molecular heats, but in the refraction equivalents, and most strikingly in molecular volumes. Kopp showed that the molecular volume of a liquid at its boiling-point is the sum of two parts solely dependent on the nature of each component, and constant for each element in similar compounds. The law, however, is only observable when the bodies are compared in similar physical states, and hence it could not be well applied to solids until Nicol made the important step of comparing them in dilute solution. He then found that there exist constant differences of volume in solution between the salts of two metals with different radicals.† Thus—

$(K-Na)Cl = 10{\cdot}0$ to $10{\cdot}48$
$(K-Na)NO_3 = 10{\cdot}39$ to $10{\cdot}44$
$(K-Na)OH = 10{\cdot}66$ &c.

The same thing is true of salts of a pair of radicals with different metals. Favre and Valsen have also noticed the existence of these constant differences under the name of density moduli. The conclusion Nicol drew from these facts is that in solution the volumes of the compounds are the sum of two parts peculiar to the components and constant for each radical in whatever compound.

Now similar constant differences have been known since the time of Andrews, Favre, and Silbermann as thermic moduli of substitution.

Attention was again drawn to these by Tommasi in 1882. It was found that there exist constant differences between the heats of formation in solution of various metals with the same pair of radicals. Thus—

| | | | |
|---|---|---|---|
| $H[Cl-Br]Aq = 10{\cdot}945$ | | $H[Cl-I]Aq = 26{\cdot}145$ | |
| K ,, ,, | $= 10{\cdot}940$ | K ,, ,, | $= 26{\cdot}150$ |
| Na ,, ,, | $= 10{\cdot}930$ | Na ,, ,, | $= 26{\cdot}150$ |
| $\frac{Ca}{2}$ ,, ,, | $= 10{\cdot}940$ | $\frac{Ca}{2}$ ,, ,, | $= 26{\cdot}150$ |
| $\frac{Sr}{2}$ ,, ,, | $= 10{\cdot}940$ | $\frac{Sr}{2}$ ,, ,, | $= 26{\cdot}150$ |
| $\frac{Cu}{2}$ ,, ,, | $= 10{\cdot}940$ | $\frac{Cu}{2}$ ,, ,, | $= 26{\cdot}150$ |

Favre and Silbermann, and Tommasi, applied these facts to the prediction of heats of formation then unknown experimentally, but the law has not yet advanced beyond this empirical stage.

A similar constancy of difference is observable if we compare the salts of different radicals with the same pair of metals. Thus—

| | |
|---|---|
| I $[K-Na]Aq = 4{\cdot}660$ | I $\left[\frac{Sr-Ca}{2}\right]Aq = 4{\cdot}020$ |
| Cl $[K-Na]Aq = 4{\cdot}650$ | Cl ,, $= 4{\cdot}020$ |
| Br $[K-Na]Aq = 4{\cdot}620$ | Br ,, $= 4{\cdot}020$ |

The above data are taken from Muir's "Thermal Chemistry," but the only conclusion he draws from them is that they are fitted to throw light on the differences between the affinities of the bodies concerned ("Principles of Chemistry," p. 450).

* Read before the University College, London, Chemical and Physical Society, March 3rd, 1887.
† CHEMICAL NEWS, vol. xlix., No. 1261.

Lothar Meyer, in an article on the Foundations of Thermo-Chemistry (see CHEMICAL NEWS, vol. xlvii., p. 265), shows that with regard to heat of neutralisation it "consists always of two parts, the one depending only on the nature of the acid and the other on that of the base." This he draws as a conclusion from the law of Andrews, that the difference between the heat of neutralisation of two acids is constant whatever the nature of the base. I wish to show that this statement is true not only of heats of neutralisation of acids and bases, but is widely applicable to all cases of combination in solution; and thus we may obtain a generalised form of the law of moduli of substitution. From the existence of these constant differences we may evidently draw a provisional conclusion similar to Nicol's,—to wit, that the heat of combination of a compound is the sum of parts peculiar to the components and constant for each atom or radical. If this be true we may speak of the *heat of combination* of an element without further qualification, since this is independent of the body with which it is combined. Each atom should have a constant *thermal equivalent* just as it has a constant refraction equivalent, or a constant atomic volume, when compared under similar conditions. The object of the present paper is to draw the attention of chemists to the existence of this general and fundamental law of Thermo-Chemistry, to calculate, as far as possible, the thermal equivalents of each element, and to apply the law to the elucidation of the phenomena of neutralisation.

The term calorific equivalent was originally applied by Favre and Silbermann to the heat disengaged by the action of equivalent quantities of halogens upon each metal, and varied according to the nature of the halogen. I propose to apply the term thermal equivalent to the constant heats of combination which I shall show to be calculable for each element.

The data above quoted will not enable us to calculate the actual thermal equivalents of the elements, because there are always more unknowns than equations. The following reactions, however, will suffice:—

$[H,Cl]Aq = 39{\cdot}315$ $[H,Cl,Am]Aq = 53{\cdot}691$
$[4Am,3Cl] = 124{\cdot}661.$

Now assuming the truth of the law that the radicals liberate or absorb the same amount of heat in all cases, we may write $H + Cl = 39{\cdot}315$, $H + Cl + Am = 53{\cdot}691$, $3Cl + 4Am = 124{\cdot}661$, whence we get $H = 16{\cdot}963$, and $Cl = 22{\cdot}352$.

Again, knowing $Aq[H,Br] = 28{\cdot}370$, we may by hypothesis put $H + Br = 28{\cdot}370$, whence Br is 11·407.

In a similar way we get $I = -3{\cdot}793$.

Again, from the heats of formation of the chlorides of various metals, we may easily obtain their thermal equivalents. Thus the heat of formation of calcic chloride being 187·600, we may put $Ca + 2Cl = 187{\cdot}600$, whence we find the thermal equivalent of $Ca = 142{\cdot}896$. In this way I have calculated the thermal equivalents of Li, Na, K, Ca, Sr, Ba, Mg, Cd, Zn, Al, Ni, Co, and Cu".

Now if the above law is true we ought to be able to calculate the heat of formation of the bromides or iodides of any of these metals by simply adding their thermal equivalents. The following are a few of the experimental and calcalated results:—

| Calculated. | | Experiment. | |
|---|---|---|---|
| K+Br | = 90·225 | Aq[K,Br] | = 90·230 |
| Na+Br | = 85·565 | Aq[Na,Br] | = 85·580 |
| Ca+2Br | = 165·700 | $Aq[Ca,Br_2]$ | = 165·800 |

The thermal equivalents of the metals are given in a Table at the end, and will be found to give results with close approximation.

Ferrous iron from the chloride is 55·246, and this gives correct results with the iodide and bromide. The thermal equivalent of ferric iron is, however, quite different, being 60·669. So with thallous thallium, Tl' = 16·128, while thallic Tl''' = 22·229; and stannous tin, Sn'' = 36·436, while stannic Sn'''' = 67·762.

The valency of a metal, therefore, has an influence on its thermal equivalent, an increase of valency being in each case associated with an increase of heat of combination. It is not therefore strictly correct to say that the heat of combination of an element is quite independent of the way in which it is combined. It is, however, constant in similar classes of compound. The same qualification is necessary in speaking of refraction equivalents or atomic volume. Hence we may speak of the thermal equivalent of ferrous or ferric iron, since it is constant in each class. So in the case of tin, &c., we must mention whether the tin be stannous or stannic.

Oxygen has a thermal equivalent which is constant in the hydrates. Thus $Aq[K,O,H] = 116{\cdot}460$, whence—

$$O = [K,O,H] - (K+H) = 20{\cdot}679.$$

Dealing thus with the hydrates of sodium, lithium, thallium, barium, strontium, and calcium, I find that in all these oxygen has a value approximately constant, and of mean worth 20·645. The following table gives a few of the calculated results to show the nature of the approximation:—

| | Calculated. | Experiment. | Error. |
|---|---|---|---|
| NaOH .. | 111·766 | 111·810 | |
| LiOH .. | 117·406 | 117·440 | |
| TlOH .. | 53·746 | 53·760 | |
| $BaO_2H_2$ .. | 226·812 | 227·120 | 0·13 per cent. |

In the oxides of the above metals oxygen has a value constant, but different from that in the hydrates, and of mean value 6·830. This yields results such as the following:—

| | | |
|---|---|---|
| $Na_2O$ .. | 155·140 | 155·260 |
| $Li_2O$ .. .. | 166·350 | 166·520 |
| SrO .. .. | 157·610 | 157·780 |

Sulphur in the sulphydrates and sulphides has a thermal equivalent constant for each class, but differing like those of oxygen, both, however, being large negative quantities:—

| | |
|---|---|
| S in sulph-hydrates .. .. | −30·520 |
| S in sulphides .. .. .. | −44·444 |

It is curious that sulphur and oxygen should have different values in the two classes of compound, since in both they are apparently similarly united.

In the sulphates, sulphur has also a constant thermal equivalent. In calculating this value we are met with the difficulty as to whether the hydroxylic oxygen has the same value as the unsaturated oxygen. I have used the value 20·645 for saturated oxygen, as in K−O−H, and 6·830 for unsaturated oxygen, as in Ca=O, perhaps somewhat unwarrantably. However, this does not affect the constancy of the number, which comes out as 125·536. Using this value we may calculate the heat of formation of any sulphate, thus:—

| | Calculated. | Experiment. | Error. |
|---|---|---|---|
| $Na_2SO_4$ .. | 328·802 | 329·050 | 0·07 per cent. |
| $Li_2SO_4$ .. | 340·280 | 340·220 | |
| $Tl_2SO_4$ .. | 212·842 | 212·700 | 0·06 ,, |
| $CaSO_4$ .. | 323·382 | 322·810 | 0·11 ,, |
| $MgSO_4$ .. | 322·682 | 322·590 | |
| $ZnSO_4$ .. | 248·582 | 248·500 | |

So also with the sulphates of Ba, Cd, Co, Ni, Fe" and Cu".

The acid itself, however, $H_2SO_4$, calculated on this basis does not agree. $Aq[H_2,S,O_4] = 210{\cdot}770$, while $H_2 + S + O_4 = 214{\cdot}412$, thus showing a difference of 3·642. The same is true with water, $[H_2,O]Aq = 68{\cdot}360$, while $2H + O = 54{\cdot}571$. It thus seems that water differs from all other hydrates, and hydric sulphate from all other sulphates, in this respect. Thus the elements of water absorb 13·789 calories less on decomposition from metallic hydrates than they evolve on re-combining to form water.

Again, sulphuric acid absorbs 3·642 calories less on decomposition than its elements evolve on re-composition to form metallic sulphates. Whatever may be the cause of this curious difference it has, as we shall see, a most vital bearing on the very existence of the phenomenon of heat of neutralisation.

When we calculate the thermal equivalent of nitrogen in the metallic nitrates, we find that it has two values in two different classes of nitrates. The nitrates of the dyad metals are sharply marked off from those of the typical monad metals. Using values for saturated and unsaturated oxygen as in the sulphates, we find that in the nitrates of the monad metals, potassium, sodium, and thallium, nitrogen has a constant value $= -12{\cdot}210$, while in those of the dyad metals, Ca, Sr, Mg, Cd, Zn, Ni, Co, Cu", it has a value approximately constant but only $= -2{\cdot}196$.

The cases of lithium and silver nitrate are peculiar: they both appear to belong to the second class rather than to the first, for the thermal equivalent of their nitrogen agrees with that in the dyad and not in the monad nitrates. Hence they would appear to be $Li_2N_2O_6$ and $Ag_2N_2O_6$, their formula being double that usually accepted. Calculated on this theory the heat of formation of lithium nitrate comes out 224·014, observed 223·830, error 0·08 per cent. The value for lithium used here gives correct results with the bromide (calculated 91·305, experiment 91·315), and with the iodide (calculated 76·105, experiment 76·100).

The thermal equivalent of silver cannot be got from the chloride or iodide, since these are insoluble in water. But calculated from the sulphate we get $Ag = -8{\cdot}843$. This gives for the heat of formation of silver nitrate, on the hypothesis that it is $Ag_2N_2O_6$, the number 46·532, observed 46·600. Hence we may infer that the molecular weight of silver nitrate is double the usually accepted number. That this is the case is not improbable from the position of silver in the periodic system, following a transition series, and being usually a pseudo-monad. Confirmation amounting to proof of this has been recently furnished by Ditte's preparation of the salts $AgKN_2O_6$, $AgRbN_2O_6$, $AgAmN_2O_6$ (*Ann. Chim. Phys.* (6), viii., 418), in which one of the silver atoms of $Ag_2N_2O_6$ is replaced by an alkali metal.

Again, lithium being one of the so-called "typical elements," it is not surprising that it should differ from the other alkali metals. The following exhibits a few results of calculation on the nitrates:—

| | Calculated. | Experiment. | Error. |
|---|---|---|---|
| $NaNO_3$ .. | 96·252 | 96·220 | |
| $TlNO_3$ .. | 38·223 | 38·210 | |
| $SrN_2O_6$ .. | 215·214 | 215·200 | |
| $MgN_2O_6$ .. | 206·414 | 206·300 | |
| $ZnN_2O_6$ .. | 132·314 | 132·330 | |
| $CdN_2O_6$ .. | 115·810 | 116·120 | 0·2 per cent. |

The data for the dithionates are also to hand. I find that in these sulphur has a constant value approximating to 88·352.

The results agree well with K, Na, Sr, Ca, Cu, Mg, and also with hydrogen, but not with nickel and silver, in which the value appears to be between 84·000 and 83·000. In the halogen salts of ammonium, nitrogen has a constant thermal equivalent, −18·294. In the alkaline carbonates, carbon is about 95·604, differing from that in $CO_2$. In chloric acid the thermal equivalent of Cl is −27·315, the same as that in potassic chlorate; and in the alkaline bromates and iodates the values of bromine and iodine are constant, and respectively $Br = -38{\cdot}835$ and $I = +4{\cdot}559$. These figures may be accepted as evidence that the halogens have not the same valency in the chlorates, &c., as in the chlorides, bromides, and iodides. This may serve to put the last straw on the back of those absurd linked oxygen formulæ which may still be seen bobbling along the pages of text-books.

It is only fair to mention here the few apparently anomalous results. The thermal equivalent of manganese is doubtful, from the nitrate 83·322, from the sulphate 83·286, from the iodide 82·586, while from the chloride only 73·296. Again, Au''' from the chloride −39·786, but from the bromide, 29·231. Lead from the chloride 31·266, from the bromide 31·696, but from the nitrate 33·672, and the dithionate 32·896.

Let us now turn to the phenomena of neutralisation in the light of this law. The reaction—

$$KOH + HCl = KCl + H_2O$$

thermally expanded is—

$$Aq[KOH,HCl] = Aq[K,Cl] + Aq[H_2,O] - Aq[K,O,H] - Aq[H,Cl]$$

The reaction consists of a re-distribution, during which each atom undergoes a decomposition and a re-composition. If, according to the above law each atom evolved, on combination, as much heat as it absorbed on decomposition, the effect of each would be nil, and the neutralisation of an acid by a base would be attended by no thermal change. But here comes the importance of the fact before noted, that the elements of water evolve 68·360 calories on re-composition, as against only 54·371 absorbed on decomposition. Hence, while the total effect of all other atoms is nil, that of the elements of water in their re-distribution is an evolution of 13·789 calories. From this we draw the following inferences.

(1) The very existence of the phenomenon of heat of neutralisation of a basic hydrate by an acid is due to the abnormal behaviour of water. Did the elements, in uniting to form water, evolve the same amount of heat as in all other hydrates, there would be no such thing as heat of neutralisation.

(2) Other things being equal, the heat of neutralisation should depend solely on the amount of water liberated in the reaction. Hence, since monobasic acids liberate one molecule of water, and dibasic acids two, it follows:—

(3) That all monobasic acids should, *ceteris paribus*, have the same heat of neutralisation, equal to the difference between the theoretical and actual heat of formation of water, *i.e.*, to 68·360 − 54·571 or 13·789.

(4) That dibasic acids should have a constant heat of neutralisation, equal to twice that of monobasic acids, or 27·578 cals.

These conclusions are well known to be true for hydrochloric, hydriodic, hydrobromic, and nitric acids, with all basic hydrates, also for bromic, iodic, and chloric acids, in which, as I have shown, the halogen has the same thermal equivalent as in the metallic salts. Their heat of neutralisation is about 13·780.

It is true of the dibasic acids, dithionic, selenious, chloroplatinic, and fluosilicic acids, whose neutralisation heat is about 27·000 cals.

In the case of sulphuric acid, as we saw, before the decomposition of its elements absorbs only 210·770 cals., while their re-composition evolves 214·412, or rather more, since its hydrogen goes to form water. Hence, when sulphuric acid neutralises a basic hydrate, in addition to the 27·578 cals. due to the water liberated, there are 3·642 cals. due to the re-distribution of the elements of the acid. This would make the heat of neutralisation of sulphuric acid 31·220, the average number by experiment being about 31·347.

In the same way the reaction—

$$Na_2O_2H_2 + CO_2 = Na_2CO_3 + H_2O$$

frees one mol. of water, equivalent to 13·720 cals. But the decomposition of $CO_2$ absorbs −102·840 cals., while the re-composition of these elements in sodic carbonate evolves 109·329. Hence we have an additional 6·489 cals. to add to the 13·720, which makes the heat of neutralisation 20·209; obverved, 20·180. So with—

$$SH_2 + NaOH = NaSH + H_2O$$

we have the decomposition of $SH_2$ absorbing −9·300, while the re-composition evolves only 3·295, the total

effect being −6·005. This we have to subtract from the 13·720 liberated by the water, giving 7·715 for the heat of neutralisation; observed, 7·740.

Hence it appears that the law to which attention has been directed in this paper is a generalisation of both the empirical laws of Andrews and of the moduli of substitution. Both these laws are included under it, and it may be stated thus:—*In similar compounds an atom evolves or absorbs on combination in solution an amount of heat which is constant whatever the nature of the body with which it combines,** or every atom has a constant thermal equivalent *under similar conditions.*

If the thermal equivalents of the atoms A, B, and C be respectively $\alpha$, $\beta$, and $\gamma$ in a given class of compounds, then the heat of formation in solution, H, of any compound A$x$ B$y$ C$z$—

$$H = x\alpha + y\beta + z\gamma.$$

Hence with a table of thermal equivalents we easily calculate the heat of formation of any required compound. The old law of moduli enabled us to do this, but being an empirical and approximate law, Berthelot, if I remember rightly, condemned it as belonging to a past period of chemical science. But when rightly understood it forms the basis of the law of constant thermal equivalents as above enunciated, and this taken in conjunction with the constant refractive equivalents, atomic volumes, and heats, and Ostwald's work on affinity, seems to me to be of the utmost theoretical importance. Every heat change during a chemical reaction probably consists of a primary part *obeying the above law*, and of secondary physical changes from which, except in solution, we cannot separate it.

What is now needed for the further generalisation of the huge masses of thermo-chemical data, is a study of the attendant physical changes. Accordingly it is to experiments on the relation of the heat change to the change in the amount of disgregation during such physical processes as fusion, evaporation, and solution that we must look for help. An attempt to find the relation between the heat of fusion and amount of disgregation was made by myself some years ago (Chemical News, vol. xlix., 1260) which, though I cannot regard it as very successful, is still, I believe, a step in the right direction.

There is evidently plenty of room for experimental research in this direction, and also on the heat of solution of organic bodies in liquids other than water. In this way we should find the heat of formation of organic bodies in solution, and thus apply the law to them also.

In conclusion I may mention that the thermal equivalent, like the atomic volume, &c., appears to be a periodic function of the atomic weight.

*Table of Thermal Equivalents.*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | = 16 963 | | | | | | |
| Li | 79·898 | Cl′ | 22·352 | Cu″ | 18·006 | Al‴ | 170·769 |
| Na | 74·158 | Br′ | 11·407 | Ag′ | −8·825? | | |
| K | 78·818 | I′ | −3·793 | Au | ? | Tl‴ | 22·229 |
| Zn | 68·096 | | Fe″ 55·246 | | Mg | 142·196 | |
| Cd | 51·596 | | Co 50·116 | | Ca | 142·896 | |
| Hg | 15·156 | | Ni 48·996 | | Sr | 150·996 | |
| Fe‴ | 60·669 | | Mn 83·300? | | Ba | 151·596 | |
| C | 95·600 | | Sn″ 36·436 | | Tl′ | 16·128 | |
| Sniv | 67·762 | O in hydr. 20·645 | | S in MSH | | −30·520 | |
| Pb | 33·672? | O in oxides 6·830 | | S in $M_2S$ | | −44·444 | |
| S in sulphates | | 125·536 | In dithionates | | | 88·352 | |
| N in ammonium salts | | | −18·294 | | | | |
| N in $MNO_3$ | | −12·210 | In $M''N_2O_6$ | | | −2·196 | |
| C in carbonates | | | 95·600 | | | | |
| Clv in chlorates | | | −27·315 | | | | |
| Brv | | −38·835 | Iv | +4·559 | | | |

* This statement is perhaps objectionable, as appearing to attribute the heat evolved to each atom separately instead of to a joint action and reaction. To avoid such an implication it would be better simply to state that the *heat of combination of a compound is separable into parts constant for each element (under similar conditions), and these constants are called the thermal equivalents of the atoms in a given class of compound.* This is a statement merely of fact, and independent of any theory.

In offering the above Table I do not regard the numbers as final, but many, especially those for the variable non-metals, may have to be modified as we understand the law better. In using them I do not think we make any theoretical assertion other than that implied in the use of the similar refraction equivalents and the so called "atomic volumes." They at present simply indicate that the heat of combination due to the action and reaction of atoms is separable into parts constant under certain conditions for each element, and these parts are the above thermal equivalents.

It is difficult to form a true scientific concept of such a separation, but this only adds to the importance of such a possibility, and this paper, it is hoped, will draw the attention of chemists to a fact which ought not to be overlooked in attempting to ascertain the true nature of the changes in heat-energy which accompany chemical action.

## NOTE ON THE DETERMINATION OF THE TOTAL NITROGEN IN ORGANIC MATTERS.

By M. RAULIN.

The Dumas procedure is certainly the most accurate method of determining nitrogen in organic substances, and it has the advantage of being applicable for nitrogen in all its states. But in its original form it is neither sufficiently expeditious nor practical for the daily operations of an analytical laboratory.

The author has sought to render it as simple and as rapid as the most practical methods, without sacrificing anything of its accuracy and its generality. The apparatus is composed of the following portions.

1. An apparatus for generating carbonic acid, on Deville's continuous system, from marble and pure hydrochloric acid, followed by two washing-bottles, one with marble and the other with sulphuric acid. The two recipients for marble and acid should have at least a capacity of 3 litres, and the delivery tube issuing from the marble-bottle must be connected by a caoutchouc tube to another tube reaching to the bottom of the acid-bottle so as to liberate there slowly carbonic acid, which expels nitrogen and oxygen; a Mohr's pinch-cock regulates this current, and a bulb tube prevents the external air from entering into the acid bottle whilst allowing the carbonic acid to escape freely.

2. This apparatus transmits a current of carbonic acid (regulated by means of two Mohr's pinch-cocks) through the combustion-tube. This is a tube of copper, 1·80 metre in length, 18 m.m. in diameter, and 3 m.m. in thickness. It is surrounded with four brass jackets, between which and the combustion-tube there is an interval of 5 m.m. Each of these jackets is 10 c.m. in length, and is fitted with two tubulures, by which the jackets communicate one with another through caoutchouc tubes. The first jacket communicates with a water-tap, and the last is fitted with a caoutchouc tube for the escape of the water. Two of these jackets are at the ends of the central tube, whilst the two others are placed equidistant in the intervening space. During the operation all four are traversed by a current of cold water to cool the central tube.

3. This central tube communicates at its free extremity by means of an escape tube with a small trough of potassa half saturated; this trough is about 40 c.m. in height. The solution of potassa is covered with a thin layer of petroleum in order to diminish carbonisation by the air. Upon this vat, held by the jaws of a support, there are two tubes graduated to 100 c.c. Into the potash plunges a pipette with two branches, the one capable of connection with each graduated tube, and the other fitted with a bulb.

4. A small furnace, of 25 c.m. in length, serves to heat in succession each of the intervals of the central tube

between the jackets. It can be withdrawn without disturbing the combustion-tube. For this purpose it is merely necessary to remove the tiles on one side and to let down two hooks at the end.

To use the apparatus we introduce into the tube a spiral cylinder of copper wire gauze, of a diameter equal to the internal diameter of the tube, and of the length of 6 c.m., so that its anterior extremity may be 10 c.m. from the anterior jacket; then, by means of a long and perfectly dry glass tube-funnel we introduce 60 grms. of oxide of copper in small grains; then we introduce the mixture of the organic matter and oxide of copper; the weight of the organic matter must be such as to yield from 60 to 80 c.c. of nitrogen. It is mixed at first with a little oxide of copper in powder and 20 grms. of oxide in grains to 8 decigrms. of the material. The funnel is then rinsed out with a little oxide in grains.

In the same manner we introduce a sample of another organic matter in the second interval of the tube between the second and the third jacket, with a second cylinder of copper gauze and oxide of copper.

Lastly, a third sample is introduced into the third interval.

The tube is then put in its place, a current of carbonic acid is passed in to clear the tube, and when the residue of the gas, not absorbable by caustic alkali, which enters the first graduated tube does not exceed ½ c.c. in a quarter of an hour, we let the current of water pass through the jackets; the gas of the graduated jar is absorbed by the pipette and the combustion of the first sample is effected, working from the front backwards, and taking no precaution beyond decomposing completely all the material and not developing the gas too abundantly at once.

When the residual gas no longer appears to increase we stop, with the first Mohr's pinch-cock, the current of carbonic acid, wash the gas in the graduated jar with the alkali of the pipette and read off. The gas is then absorbed with the pipette and the development of gas is continued. We make ourselves then certain that the residue obtained in a quarter of an hour does not exceed ½ c.c. This residue is then measured by adding it to the previous volume; we note the duration of the operation, and read off the volume of the gas in the second graduated jar, after having washed it by means of the alkali of the pipette. We then pass on in the same manner to the combustion of the second sample after having absorbed the gaseous residue with the pipette. After completing the third sample carbonic acid gas is passed through for half an hour and the gaseous residue is measured.

To calculate the weight of nitrogen of one of these samples we deduct from the total volume of nitrogen obtained for this sample the volumes of oxygen and nitrogen liberated by the carbonic acid alone during the time of combustion.

Let V be the volume of gas thus corrected, let $v$ be the volume of permanent gas of the second graduated jar, and $p$ the weight of nitrogen of the same volume under the same conditions. The weight of nitrogen sought for will then be—

$$p \cdot \frac{V}{v}$$

It is sufficient to calculate $p$ once for all. For this purpose, before the experiment, the second graduated jar is washed with water, stoppered loosely with a stopper fitted with a thermometer, and left to itself for some time near the alkali trough; the temperature, $t$, is read off, the graduated jar is placed suitably over the potash, the volume, $v'$, of the gas, the barometric pressure, H, is read off, and the equivalent height, $h$, of the mercury. Lastly, the maximum tension, F, of watery vapour at the temperature $t$ is found.

We have then—

$$p = 1{\cdot}3 \text{ m.gr.} \times 0{\cdot}972 \times v : \frac{1}{1 + at} \times \frac{H - h - F}{760}$$

—*Bulletin de la Soc. Chimique de Paris* (xlvii., No. 2, p. 94).

## A CONVENIENT SUBSTITUTE FOR SEALED TUBES FOR HEATING UNDER PRESSURE.

By ARNOLD EILOART, B.Sc.

This device arose from a special difficulty in the heating of ether under pressure. 150 c.c. of ether, with an equal volume of an aqueous solution, were heated to 100° in a soda-water bottle, closed with a dense cork wired down. On cooling, the cork was found unmoved, but nothing was to be seen in the bottle, though it was mouth downwards under water. The ether had so attacked the cork, though the aqueous solution was between, that crystals of salt from the solution were found in the body of the cork, which had also shrunk, but not enough to admit water on cooling, so that the bottle finally contained ether vapour and air only.

A soda-water bottle with ball-stopper was tried, with mercury to prevent the ether attacking the caoutchouc ring against which the ball presses to close the bottle. The difficulty was to close the bottle so filled, seeing that ordinarily, when the bottle closed by the thumb is inverted, the glass ball floats on the mercury: the bottle closed by the thumb was gradually inclined till the ball just rolled into its place, when the bottle was promptly inverted and the thumb at the same time removed. In this way, after a few trials, closure may be effected every time with the escape of only a few drops of liquid and not a drop of mercury. The bottle, still inverted, and having an inch or two of mercury in the neck, was boiled, and found in repeated experiments to stand the pressure of the ether perfectly. Moreover, the necessity of corking and wiring is avoided.

To prevent negative pressure, and consequent displacement of the ball, the bottle should be kept warm until it is to be opened.

King's College Laboratory,
March, 1887.

## ON THE VARIATIONS OF THE ABSORPTION SPECTRA OF DIDYMIUM.

By HENRI BECQUEREL.

In a communication recently made to the Academy (*Comptes Rendus*, civ., 165) the author has shown that among the absorption-bands of the crystalline compounds of didymium, a certain number present, in their principal directions of absorption, differences which seem to reveal the existence of as many distinct substances.

Observations of another order lead to the same conclusions. If we compare with each other the absorption-spectra of different crystals, natural or artificial, containing didymium in the state of different combinations (parisite, monazite, apatite, scheelite, strontianite from Scotland, leucophane, didymium sulphate, double didymium or lanthanum nitrates with potassium, ammonium, zinc, &c.), we find that there exist in these spectra a great number of bands whose aspect is characteristic. But their different relative distances or the wave-lengths of the radiations observed vary from one body to another. On comparing the spectra of these crystals two by two we see, for instance, an entire series of bands displaced in one direction, whilst another series remains fixed; these series vary from one body to another, so that almost all the bands are individually displaced by quantities variable in one direction or in the other.

Occasionally certain bands are wanting, the substances which produce them having been eliminated either in natural crystals, or in the chemical operations by which the matters studied have been obtained.

Variations of the same kind are observed on dissolving water one of the artificial crystals mentioned above. In this case we may, before dissolving the crystal, identify all the absorption-bands and seek to find them again in the solution. As in this we observe the superposition of the principal different absorption-spectra of the crystal, the bands which in the crystal disappear, for certain directions of the luminous vibrations will be more or less weakened in the spectrum of the solution; further, certain bands lose their definiteness in consequence of the juxtaposition of several neighbouring bands belonging to different principal spectra. Excepting these modifications, which are generally easy to recognise, we find in the solution the chief bands observed in the crystal; but among these bands some remain fixed whilst others are unequally displaced in one or the other direction.

In a table the author gives the approximate wave-lengths of some of the absorption bands which present the most distinct variations between the spectra of the crystals and those of their concentrated aqueous solutions. In this table there are found neither the bands of the red region nor the numerous bands of the characteristic group near D between the wave-lengths 598 and 574, for which the multiplicity of the neighbouring bands does not permit us to follow distinctly the displacement of each.

In the table the author gives the comparative wave-lengths and the displacements for the crystals and the solutions of didymium sulphate, didymium and potassium nitrate, and lanthanum and potassium nitrate. The bands from 571·7 to 511·5 are referred to neodymium; those from 482·3 to 446·5 to praseodymium; and that of 428·5 to neodymium.

It is noted that whilst some of the bands are unaffected others are displaced considerably in one direction or in the other.

Similar variations are not observed with well-determined bodies; thus, with the various compounds of uranium, every modification which, from a chemical combination or the solution of the crystals affects one of the bands, affects at the same time all the others in the same manner. It is the same if we dissolve certain colouring-matters in the various solvents: all the bands are displaced at once in the same direction.

The phenomena presented by didymium may be explained if we admit that each of the variable bands belongs to a distinct substance. If in these various combinations each of these substances behaves differently, if each in the state of sulphate or nitrate becomes more or less hydrated according as it is in presence of one salt or of another, we see that the corresponding bands must undergo individual modifications analogous to those observed. It is necessary to add that precisely differences of this order in their chemical properties have enabled several groups of these bodies to be separated.

The observation of the unequal displacements of the bands under the conditions indicated above furnishes us, therefore, with a method for characterising substances chemically different.

We find thus that most of the bands given in the table may be ascribed to different substances, in particular the three bands of praseodymium, 481·9, 469·0, 445·0, the group 475 5; then the bands of neodymium, 571, 523·9, 521·4, 520·5, 511·5, 427, without including other bands in the red region and in the group near D; these wave-lengths refer to the solution of the nitrate. It is remarkable that the spectra of the solutions of the various double nitrates are all identical, although the spectra of the crystals of these double nitrates present very striking differences; it seems that the double compound is destroyed in dissolving. The bands just enumerated are precisely those which in the crystals have particular principal directions of absorption, and of which several groups have been separated chemically.

These bands present, therefore, at once a crystalline individuality and a chemical individuality. Still we cannot yet decide if the matters producing them are really all distinct simple bodies. It is not doubtful that the absorption-bands mentioned are due to matters presenting a certain number of the properties which characterise simple bodies, but it may also be that a certain number of these matters are combinations of one and the same substance either with some other substance or with itself, and that these combinations are so stable that hitherto one has not been transformed into another. In this case the variations of the absorbent properties would be quite analogous to those which the author has observed in the uranous and uranic compounds.

Lastly it must be noted that the wave-lengths of the characteristic bands of these different substances present, among themselves, certain relations which seem to attach them to a common origin. To this question the author proposes shortly to return.—*Comptes Rendus*, civ., p. 777.

## THE POST-MORTEM DETECTION OF CHLOROFORM.*

By CHARLES LUDEKING, Ph.D.

In an important trial for murder recently held in St. Louis, the author of this paper made a chemical examination of the viscera of the victim, at the request of the coroner, and obtained very decided reactions for chloroform, notwithstanding the fact that the examination was not undertaken until about twelve days after death. The lungs, usually congested in case of death by chloroform, were selected as best suited for its detection. The great volatility of chloroform would seem *a priori* to preclude the possibility of its detection so long after death, and as at the time there was considerable doubt expressed as to the reliability and accuracy of the experiments, the author determined, once for all, to decide the matter by direct experiment, and so set to rest all doubts.

The literature was first scanned carefully to ascertain whether there were any prior experiments in this direction, but nothing could be found. My direct object was then to determine how long after death chloroform can, with certainty, be detected; as also whether or no any substances are generated by the process of decomposition, which might give similar reactions to chloroform, and thus lead to erroneous conclusions.

The manner of experimenting was simple and direct. Dogs of from 15 to 20 pounds weight were destroyed gradually by the administration of chloroform through the lungs in from 5 to 10 minutes. Then the carcases were allowed to stand in summer's heat or the temperature of the room for different periods of time, and finally the lungs removed and tested for chloroform, by the Ragsky method.† In the following the experiments are briefly given.

### *Experiment* I.

Carcass exposed on a dissecting table, during full summer's heat, for six days and ten hours. Decomposition far advanced and an exceedingly offensive odour given off. The lungs were removed, and after having been finely minced and rendered *slightly* alkaline by means of sodium carbonate, were heated over a water-bath in a flask through which a current of air was slowly passing. The escaping gases were sent through a Bohemian glass tube, which was heated to bright redness over a space of 2 inches. The iodised starch paper was 5 inches distant from this heated portion of the tube, and throughout the experiment remained perfectly cool.

A very strong blueing of the paper was observed, and the nitrate of silver solution was strongly precipitated.

### *Experiment* II.

Carcass exposed during full summer's heat for ten days. It had then lost all solidity, the hair literally falling off by

* Presented before the St. Louis Academy of Science, June, 1886.
† *Erdmann's Journ.*, xlvi., 170.

the slightest abrasion. The lungs were removed and examined as in Experiment I. A very decided reaction for chloroform was obtained.

*Experiment* III.

Carcass exposed during full summer's heat for ourteen days. The lungs then removed and examined as in Experiment I. The reaction for chloroform was very decided.

*Experiment* IV.

Carcass placed in an ice-chest for three weeks, and then exposed for ten days during full summer's heat. The lungs were then examined as in Experiment I., and a strong reaction for chloroform obtained.

I do not hesitate to say that in winter chloroform could be detected without the slightest difficulty for many months after death.

*Experiment* V.

Carcass exposed in a room (70° F., very constant) for three weeks and three days. The lungs were then examined as in Experiment I., and a very decided reaction for chloroform obtained.

*Experiment* VI.

Carcass exposed in a room (70° F., very constant) for four weeks. The lungs examined as in Experiment I., and a decided reaction for chloroform obtained.

The question now arises whether there cannot be substances formed by the process of decomposition, which, resembling chloroform in certain chemical reactions, might therefore lead to erroneous conclusions. Dr. Ragsky already partially answered this question experimentally. The author made three experiments to this end which are herewith briefly given.

*Experiment* I.

The lungs of a slaughtered bull exposed during full summer's heat for ten days. Not a trace of reaction of chloroform could be obtained by the Ragsky method.

*Experiment* II.

The lungs of a slaughtered bull exposed during full summer's heat for fourteen days. Not a trace of reaction of chloroform could be obtained by the Ragsky method.

*Experiment* III.

Carcass of a dog destroyed by coal-gas was exposed in a room (70° F., very constant) for three weeks and four days. No chloroform reaction could be obtained by the Ragsky method.

*Conclusions.*

1. By the process of decomposition no substances are generated which could vitiate the tests for chlororform by the Ragsky method.

2. Chloroform, when it has caused death by inhalation, can with certainty be detected in the body four weeks after death, and, notwithstanding its volatility, it is certainly retained in the viscera in large amount during this time.

In the case which was the cause of these experiments being undertaken, the victim had been dead at least ten days before the body was discovered, in high state of decomposition. On the strength of the Ragsky and Hofmann tests the author gave it as his sworn opinion that the deceased had chloroform in his viscera, whereupon a charge of murder by chloroform was preferred. Maxwell, the culprit, finally, after the lapse of an entire year, made confession that chloroform had indeed been the cause of death.

It being certain, finally, that chloroform can be detected a long time after death, as evidenced by our experiments, we must next try to understand why this should be so. The following may serve to this end.

R. Dubois* finds that the vapour of chloroform penetrates into the interior of the tissues, and becomes substituted for normal water. This is not a phenomenon of desiccation or osmose; a true affinity comes into play, the protoplasm absorbing the vapour of the anæsthetic and expelling a certain quantity of water.

Chancel and Parmentier† have proven that chloroform has a very decided affinity for water.

The author allowed to stand open a flask containing water, holding a small quantity of chloroform in solution After two weeks' time the chloroform reactions could still be obtained without any difficulty.

Add to the above that chloroform is a powerful preservative agent† we have a collection of factors sufficient to enable us to understand the lengthy occlusions of chloroform in the animal body, though others of minor importance might be adduced besides these.

Grehaut and Quinquand,‡ experimenting on dogs, find the amount of chloroform necessary to produce anæsthesia to be at least one grm. to every two litres of blood. On the basis of these results, the total quantity of chloroform in the blood of a man of 150 pounds weight would be 2¾ grms. approximately, when rendered insensible through its inhalation. The amount necessary to produce death would, under normal conditions, certainly not be less than this. Under the assumption that one-sixth of the entire quantity of blood circulating in the body is at all times passing through the lungs, the quantity of chloroform in the lungs of a man of 150 pounds weight, rendered insensible from its inhalation, would be about one-half grm.

We desire to emphasise by this calculation that there is an abundanee of material in the lungs for the detection of chloroform. The liver would undoubtedly also be very suitable for its detection.—*American Chemical Journal*, Vol. viii.. No. 5.

* Chemical News, liii. 311

## ON MERCUROUS HYDRATE.

By G. B. BIRD.

Since cupric hydrate is readily formed by precipitation, at common temperatures, with an alkaline hydrate, and is subsequently so easily decomposed by heat, it appeared probable that, while the oxides of silver and mercury are precipitated from their solutions by alkaline hydrates, the corresponding hydrates of these would be formed if operating at a lower temperature. Pursuing this suggestion, in this laboratory, in 1884, Mr. J. D. Bruce undertook the formation of argentic hydrate; and it appeared that in dilute alcohol argentic hydrate decomposes at all temperatures above −40° C.§ Employing a similar method, Mr. Bird has endeavoured to obtain mercurous hydrate.

A dilute solution of mercurous nitrate was mixed with alcohol, cooled to −18° C., and the small amount of salt which separated filtered off, thus obtaining 70 per cent alcohol saturated with mercurous nitrate. A similar solution of potassium hydrate was made, and in the following experiments these were used in such amounts as gave a slight excess of the potassium hydrate solution.

When mixed at common temperature these alcoholic solutions afforded the same brownish black precipitate of mercurous oxide that is obtained from aqueous solutions. Corresponding portions of these solutions were put into test-tubes, and these cooled to −37° C., and then united and mixed by stirring; a flocculent precipitate of red-amber colour was slowly formed, which subsided very slowly: as this was warmed it gradually darkened, until at −18° C. it was of a slate-grey colour, with a yellowish green portion suspended in the liquid.

Another experiment, beginning at a temperature of −39° C., afforded the same results.

* *Comptes Rendus*, c., 27.
† Robin and Augendre, *Comptes Rendus*, xxx, 52; xxxi. 679.
‡ *Comptes Renaus*, xcvii., 753.
§ Chemical News, vol. l., p. 208.

The most satisfactory experiment was made on a morning when the temperature of the atmosphere was −18° C.

The bottom of a test-tube was perforated, and the tube was then drawn out, forming a pipette, the bulb of which was at its lower end, and fitted into another test-tube, in which the potassium hydrate solution was put: by this arrangement the solution could be cooled in the pipette and transferred to the tube containing the mercurous nitrate with very little alteration of temperature. Using sufficient of one solution to correspond to one pipetteful o the other, these were cooled to −42° C. The perfectly clear though somewhat viscous liquids were then mixed. At first the solution showed only a pale yellow colour; after a minute a very pale amber flocculent precipitate formed slowly, and remained suspended in the liquid; after two hours the temperature had risen to −23° C., the main portion of the precipitate had subsided and was darkened a little, the suspended portion being yellowish green; after four hours the temperature was −18° C. and the precipitate of a dirty yellow colour; after six hours the temperature was −10° C., the colour was slightly darker and more greenish. A portion of this precipitate was collected, dissolved in cold nitric acid, and proved to contain much mercuric salt.

Judging from the colours of the corresponding compounds of lead, copper, silver, and mercury, it appears very probable that the pale amber-coloured precipitate obtained was mercurous hydrate, and that it readily decomposes by heat, forming in part mercurous oxide and water, and more largely mercuric oxide, mercury, and water.—*American Chemical Journal*, vol. viii., p. 426.

## DETERMINATION OF NITROGEN IN COMMERCIAL FERTILISERS.*

By B. B. ROSS and L. W. WILKINSON.

At a meeting of official Agricultural Chemists held in Washington, September 1 and 2, 1885, the committee on nitrogen reported that the samples sent out by the committee were so few and meagre and the discrepancies so large as to make it inadvisable to recommend any method for the determination of nitrogen for use during the next season, and recommended that the entire report of the last committee be referred, without further action, to the next committee on nitrogen. The new committee, in accordance with the report referred to, sent out other samples during the present year with specific instructions to be followed in determinations according to the Ruffle method, the one proposed by the committee for adoption by the Association. Nitrogen was also determined in the same samples, for the purpose of comparison, by the soda-lime and the Kjeldahl methods. As these determinations were made with great care, the results are believed to be of sufficient interest to justify their publication.

The reagents used in the Ruffle method consisted of standard solutious of sulphuric acid and caustic potash, one-forth normal; soda lime crushed, one-half in form of powder and one-half granular; sodium hyposulphite, commercial, fused, water-free, and powdered; finely powdered charcoal and flowers of sulphur, equal parts by weight; and cochineal solution as an indicator. The combustion tube was twenty inches in length and one-half inch in diameter.

The samples used for analysis were represented to consist of Nos. 1 and 2, ordinary commercial fertilisers containing nitrogen, No. 3, a rather superior sample of cotton-seed meal, and N. 4, a nitrate mixed with sugar.

Careful analysis of the chemicals used in the Ruffle method showed them to contain a small percentage of nitrogen which is allowed for in the following results:—

*Results according to the Ruffle Method.*

| | (*a*). | (*b*). | (*c*). | Average |
|---|---|---|---|---|
| No. 1—Nitrogen found .. | 1·83½ | 1·86 | 1·85 | 1·8483 |
| No. 2 ,, ,, .. | 2·15 | 2·16½ | 2·15 | 2·1541 |
| No. 3 ,, ,, .. | 7·66½ | 7·57½ | 7·35 | 7·53 |
| No. 4 ,, ,, .. | 3·45 | 3·39½ | 3·35 | 3·3983 |

*Results according to the Method with Soda Lime.*

| | (*a*), | (*b*). | (*c*). | Average |
|---|---|---|---|---|
| No. 1—Nitrogen found .. | 1·84 | 1·85 | — | 1·845 |
| No. 2 ,, ,, .. | 2·05 | 2·12½ | — | 2·0875 |
| No. 3 ,, ,, .. | 7·25 | 7·27½ | — | 7·2625 |
| No. 4 ,, ,, .. | 2·10 | 2·12½ | — | 2·0875 |

*Results according to the Kjeldahl Method.*

| | (*a*). | (*b*). | (*c*). | Average |
|---|---|---|---|---|
| No. 1—Nitrogen found .. | 1·85 | — | — | — |
| No. 2 ,, ,, .. | 2·17½ | — | — | — |
| No. 3 ,, ,, .. | 7·33 | — | — | — |
| No. 4 ,, ,, .. | — | — | — | — |

From eight to ten hours' digestion with sulphuric acid was required in the Kjeldahl method and about three-quarters of an hour for distillation, making it long and tedious. No. 4, consisting of sodium nitrate and sugar, yielded totally unreliable results, and is omitted. The quantity of material sent was too small to allow of other determinations.

The above determinations show the uniform and satisfactory results obtained by the Ruffle method, and commend it to the favourable consideration of agricultural chemists especially.

* "Notes of Practical Work in State Laboratory, Auburn, Alabama." Communicated by N. T. Lupton, Professor of Chemistry in the Agricultural and Mechanical College, and State Chemist.

## NOTICES OF BOOKS.

*The Economical Aspects of Agricultural Chemistry.* An Address read before the American Association for the Advancement of Science. By Harvey W. Wiley. Cambridge: J. Wilson and Son. University Press. 1886.

"The prosperity and advancement of a nation depend chiefly on its agriculture. The first and most insistent demands of a human being are for food and clothing, and for these he depends exclusively on the products of the field." In these words Mr. Wiley calls our attention in a very forcible manner to the extreme importance of agricultural chemistry, a branch of science which has until comparatively modern years been too much neglected.

In the olden times, when populations were not so large as they are at present and competition was not so great, farmers were easily enabled to grow enough wheat, &c., for the wants of the district, and the prices were fairly remunerative; but now that the demand has increased to such an enormous extent, and the importation of foreign bread-stuffs has brought down the prices, no stone should be left unturned or precaution neglected to increase the yield per acre. It has been shown over and over again that it *does* pay to use chemical manures, but for all that they are not used to anything like the extent they should be. The percentage of potash removed from the soil and found in the ash of the grain of cereals varies from 16·33 per cent in the case of oats and barley to over 31 per cent in wheat and rye, and in the straw from 13·6 per cent in wheat to 46·8 per cent in buckwheat. The percentage of phosphoric acid varies from 23 per cent to 48·6 per cent in the grain, and from 4·5 per cent to 12·6 per cent in the straw of the same cereals.

If these figures are applied to the total quantity of grain raised every year in the United States, we find the enormous totals of 4,035,586,388 lbs. of potash and 2,714,585,473 lbs. of phosphoric acid which ought to be returned to the soil every year, to keep it up to the same standard of fertility: these figures represent 28·2 lbs. of

potash and 19 lbs. of phosphoric acid per acre. The hay crop, again, removes a very large quantity of these necessary constituents, viz., 1,418,788,800 lbs. of potash and 468,795,600 lbs. of phosphoric acid.

Similar calculations are given for the other constituents of the soil, the total value of all being 3,343,786,050 dollars.

These quantities of plant-food removed rom the soil annually seem enormous, but it must be remembered that they are not all lost; much is left in the soil in roots, straw, stalks, &c.

The store of plant-food in virgin soil is of course very great, but it is quite impossible that it can withstand this constant drain for very long: that this is true is shown by the diminished yield in the great wheat-fields of California and the North-West, which do not now produce more than half the crop at first obtained from them.

In view of the fact that nitrogen is one of the most abundant of the elements, it may appear strange that so high a value is placed on it, or that there should be any question as to the abundance of the supply. There has been much discussion as to the form in which nitrogen enters into plant-life, and there is still much difference of opinion as to the possible sources. Mr. Wiley mentions organic nitrogenous matter, ammonia in the air, nitric and nitrous compounds formed by combustion, free nitrogen in the air, &c., and he goes on to consider the merits of these different views, and concludes that the combined nitrogen which is the product of vegetable and organic life forms the chief source of nitrogen for the growing plant.

Manure is not the only requisite to plant-life, a certain amount of warmth and light being quite as indispensable. "If it be true, therefore," says Mr. Wiley, "that the earth is gradually cooling, there may come a time when a cosmic athermancy may cause the famine which scientific agriculture will have prevented. Some time in the remote future the last man will reach the equator. There, with the mocking disc of the sun in the zenith, denying him warmth, flat-headed, and pinched as to every feature, he will gulp his last mite of albumenoids in his oatmeal, and close his struggle with an indurate inhospitality."

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*Notes on the Literature of Explosives.* By Charles E. Munroe. Nos. X. and XI.

The first paper noted and commented upon is one by Dr. Jenssen on the "Causes of Explosions in the Manufacture of High Explosives." These are generally traced to improper construction and faulty arrangement of the works and machines, carelessness on the part of the workmen, and maliciousness. As an example of the latter the writer cites one, from his own experience, where a quantity of tips from phosphorus matches were placed in a bag of infusorial earth, and were not discovered until the earth had been made up into dynamite.

Several papers follow on the chemistry, the composition, and the physiological action of nitro-glycerol.

In some experiments made by Berthelot, to determine the rate of transmission of the explosive wave in solid and liquid explosives, he found that as a rule the rate of propagation of the explosive wave increases with the density of loading, and also with the diameter of the tube in which the experiments were carried out, the tubes used in these cases being 1 to 2 m.m. diameter and 100 to 200 metres long. The results were sensibly the same whether the tubes were bent or straight.

Among the processes used in producing metallic potassium is that in which an intimate mixture of potassium carbonate and charcoal is heated in an iron retort. The potassium is thus reduced, but there is unfortunately another secondary reaction, through which a black compound is formed which detonates violently upon the slightest friction.

The final Report of the English Royal Commission appointed to enquire into accidents in mines is here commented upon. Not much is recommended in the way of legislative changes, but the scientific recommendations are most interesting and important.

With reference to exploding shots in mines they say—"Electrical exploding appliances present very important advantages, from the point of view of safety, over any kind of fuse which has to be ignited by the application of flame to its exposed extremity. . . . The use of electrical arrangements for firing shots in mines, where the employment of powder for blasting is inadmissible, should be encouraged as much as possible."

While engaged in the manufacture of zinc, Col. S. Wetherill devised a plan for recovering the "blue powder," or finely divided zinc, deposited in the condenser. It consisted in pressing it into blocks and melting them down into spelter. The workman in charge proposed facilitating the process by shovelling the powder direct into the hot furnace, and then ramming it down: on trying this the first shovelful exploded with great violence, and drove the blade of the shovel into the roof of the building.

There are many other papers on fulminates, &c., which are noted and commented upon.

In conclusion, we think the following extract from the *Maryland Gazette*, June 14th, 1749, is worth quoting:—"On Friday last (9th June) the gentleman who has exhibited the electrical experiments in town removed his machine off to the south side of our creek (Spa Creek?), and having set some spirits of wine in a small vessel on a table on the north side, he caused a spark of electrical fire to dart across in an instant through 200 yards of water, which set the spirits in a blaze the first attempt, and several times afterwards, and discharged a battery of eleven guns, to the surprise and great satisfaction of the spectators." The gentleman's name is not given.

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# CORRESPONDENCE.

## THE NATURE OF SOLUTION.

*To the Editor of the Chemical News.*

Sir,—In the report of the Proceedings at the last meeting of the Chemical Society, which appeared in the Chemical News, vol. lv., p. 136, Dr. Nicol is represented as stating that I have "abandoned the definite hydrate theory" of solution. Dr. Nicol misunderstands me very much if he imagines this to be the case. In a large number of cases a definite hydrate is undoubtedly formed by the addition of a small amount of water to a salt, and it has certainly not yet been proved that a further addition of water decomposes this compound; therefore, I believe that it, or some higher definite hydrate, exists in the liquid in most cases. Neither do I believe in indefinite hydrate-aggregates, as Dr. Nicol states, but in what is a very different thing, hydrates of so complex a character and so easily dissociated that our imperfect methods of investigation fail to reveal their definiteness. A belief in complex compounds of such a nature does not imply a disbelief in definite molecular compounds, any more than a belief in these molecular compounds implies a disbelief in the atomic compounds of which they are composed.

There may, perhaps, not be any great difference between Dr. Nicol's views of solution and my own, but I fear we shall not agree so long as we hold such different views as to what the hydrate theory means, and as to the nature of chemical compounds in general. Dr. Nicol appears to regard the hydrate theory to represent the solution as containing the salt in the same state of hydration as it is known in the solid state, the hydrate being perfectly stable and never partially dissociated; whereas, I take the theory simply to mean that dissolution is the result of the chemical combination of the salt with the water, the compound formed being possibly identical with the solid hydrate, but probably not so, probably much more

complex, and never entirely free from dissociation. Dr. Nicol appears to regard a chemical compound as an aggregate of molecules containing but a few atoms, always stable, and which must always necessarily give evidence of its compound nature when examined in any way, and from any point of view. I, on the other hand, admit as a chemical compound a substance which, when examined from any one point of view, gives unmistakeable evidence that it is not a mere mixture, and I know of too many instances of well authenticated compounds, which have never been isolated, which are always partially dissociated, and which, in some respects, behave as if they were mere mixtures, to accept negative evidence of this nature, as proving that this substance is *not* a compound. Dr. Nicol asks me at what number of molecules or atoms I draw the line for chemical combination. I draw a line nowhere. I have no prejudices or preconceived ideas which would stand in the way of my accepting a compound containing many millions of atoms, provided always that the evidence in favour of its being a compound were sufficiently strong.—I am, &c.,

Spencer Pickering.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 10, March 7, 1887.

**Direct Fixation of the Gaseous Nitrogen of the Atmosphere by Vegetable Earths, with the Assistance of Vegetation.**—M. Berthelot.—In the author's experiments there has taken place a fixation of nitrogen in a considerable proportion in sands and clayey soils, as well as in vegetable mould properly so-called, when he operated in the absence of vegetation, and in the soil and the plant taken collectively when the experiments are conducted in the presence of vegetation. The vegetation, however, seems to consume a part of the nitrogen fixed by the soil. The life of the higher plants, like that of animals, gives rise to an incessant loss of combined nitrogen.

**Spectra of Sparks from Thick Wire Coils.**—E. Demarçay.—In a former memoir the author has stated that the spectra in question, judging from those of the alkaline metals, are arc-spectra. This conclusion is not accurate for all substances. On comparing these spectra, in the region less refrangible than $\lambda = 330$, with those described by Messrs. Liveing and Dewar, the author finds that the spectra of potassium, sodium, thallium, and aluminium seem identical. Those of barium, strontium, and calcium seem approximately identical in the intensities of the rays. The spectra of tin, lead, and mercury, on the contrary, are very different, and do not resemble those given by Messrs. Hartley and Adeney. Judging from the visible portion they differ generally from those described by M. Lecoq de Boisbaudran.

**The Laws of Dissolution.**—H. Le Chatelier.—A reply to a memoir by MM. Chancel and Parmentier. The author recalls the fact that the law of solution which he announced is only an approximation, based upon a certain number of experimental laws more or less exact.

**Certain Formulæ relative to Saline Solutions.**—M. Duhem.—A discussion of the formulæ of Kirchhoff, Le Chatelier, and Wüllner.

**An Especial Case of Solution.**—F. Parmentier.—In general, if a solid is dissolved in a liquid, when the complete liquefaction of the solid has been effected, we may add to the solution any excess whatever of the solvent without the mixture ceasing to be homogeneous. If we dissolve phospho-molybdic acid or silico-molybdic acid in common ether it is found that at a given temperature solution takes place only between definite quantities of acid and of ether. If once these acids are dissolved in a suitable quantity of ether any excess of the solvent does not mix with the solution.

**An Acid obtained by the Action of Potassa upon a Mixture of Acetone and Chloroform.**—R. Engel.—The acid in question has the formula $C_{11}H_{20}O_6$. Its formula corresponds to the condensation of 3 mols. acetone with fixation of two groups COOH and loss of oxygen.

**Synthetic Researches on Certain Derivatives of Diphenyl.**—P. Adam.—The products obtained are diphenyl-diphenylacetone and diphenyl-methyl-carbonyl.

**Active Camphene and Ethyl-Borneol.**—G. Bouchardat and J. Lafont.—The camphene obtained in the first treatment has a rotatory power of about $\frac{2}{3}$ of that possessed by the terecamphenes already obtained. The combined action of a temperature of 150° at the outset and 175° at the end, and of acetic acid and potassium acetate, rapidly reduces the value of the rotatory power. The ethylate of camphene is probably an ethyl-borneol identical or isomeric with that of Baubigny.

**Action of Ethylene Bibromide upon the Alkaline Alcoholates: Preparation of Acetylene.**—M. de Forcrand.—A thermo-chemical paper which does not admit of useful abstraction.

**Formation-Heat of Tartar Emetic.**—M. Güntz.—This compound is produced with absorption of heat, its formation-heat being $-0{\cdot}85$ cal.

*Journal für Praktische Chemie.* New Series, Vol. xxxv., Parts 1 and 2.

**Researches from the Chemical Laboratory of Prof. Alexander Saytzeff, of Kasan.**—These investigations comprise memoirs on methoxy-diallylacetic acid and its salts by S. Barataeff; on the action of a mixture of iodallyl, iodethyl, and zinc upon oxalic ethyl-ether, by the same author, and on the acetic ether obtained by the action of silver acetate upon tetra-brom-diallylcarbinol acetate, by W. Dieff.

**Calorimetric Researches.**—F. Stohmann.—We have here two treatises; one by F. Stohmann, P. Rodatz, and W. Herzberg on the thermic value of the ethers of the phenol series, and the other, by the same authors, on the thermic value of the homologues of benzol.

**Solubility of Gypsum in Solutions of Ammonium Salts.**—S. Cohn.—The question whether the irregular solvent action of ammonium nitrate upon gypsum, observed by Haver-Droeze is a peculiarity of the ammoniacal salts must be answered in the affirmative for ammonium chloride and nitrate, but in the negative for ammonium sulphate. The cause of this difference is to be sought in the possibility of a chemical transformation with the gypsum. Ammonium sulphate increases the solubility of gypsum probably by the formation of readily soluble double salts. Ammonium chloride, nitrate, and acetate increase the solubility of gypsum by mutual decomposition, with the formation of readily soluble calcium salts; the formation of double salts comes here less into play. The action of ammonium salts capable of double decomposition with gypsum increases with decreasing concentration. The solubility of gypsum is greatest in solutions of ammonium acetate; then follow the nitrate, the chloride, and lastly the sulphate.

**Contributions to the Chemistry of Manganese and Fluorine.**—Odin T. Christensen.—The author has already communicated the main results of his researches on the manganese double fluorides. He now describes the whole investigation more fully, and in particular the behaviour of the manganese oxides with hydrochloric and hydrofluoric acids.

**The Synthesis of Kyaphenine.**— Peter Klason.—The author concludes that as kyanmethine and kyanurethine, in consequence of their analogous formation, have the same constitution as kyaphenine, the polymeric nitriles may be regarded as true cyanuric compounds.

**Remarks on the Foregoing Memoir.**—E. von Meyer. —The author rejects Herr Klason's conclusion that the three bases in question must have analogous constitutions on account of their origin.

**Apparatus for Determining Carbonic Acid and all Similar Gases.**—Prof. Dr. R. Bauer.—This paper requires the accompanying figure.

**Behaviour of Acetic Acid and some of its Derivatives with Phosphorus Pentachloride.**—A. Michael.—Not adapted for useful abstraction.

## MISCELLANEOUS.

**Chemical Society.**—At the Anniversary Meeting, held on the 30th of March, the following gentlemen were elected Officers and Council of the Chemical Society:—

*President*—W. Crookes, F.R.S.

*Vice-Presidents who have filled the office of President*—Sir F. A. Abel, C.B., D.C.L., F.R.S.; Warren De la Rue, D.C.L., F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

*Vice-Presidents*—J. Dewar, M.A., F.R.S.; David Howard; H. McLeod, F.R.S.; Ludwig Mond; C. Schorlemmer, Ph.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

*Secretaries*—H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

*Foreign Secretary*—F. R. Japp, M.A., Ph.D., F.R.S.

*Treasurer*—W. J. Russell, Ph.D., F.R.S.

*Members of Council*—T. Carnelly, D.Sc.; M. Carteighe; A. H. Church; Frank Clowes, D.Sc.; P. F. Frankland, Ph.D.; R. J. Friswell; E. Kinch; R. Messel, Ph.D.; H. F. Morley, M.A.; J. A. R. Newlands; W. Ramsay, Ph.D.; Thomas Stevenson, M.D.

**Water Analysis for 2s. 6d.**—A correspondent sends us the following cutting from the "Correspondence'" column of a weekly contemporary:—"*Analysing Water.* —If 'Midge' were quite a genius it might be worth while to tell him how to conduct this process, but it is doubtful if he would succeed the first time he tried. A more simple way would be for him to procure a new glass bottle (with a new cork) and fill it with the suspected water, take this bottle to the best chemist's shop in a good town, ask for a rough analysis, and offer 2s. 6d. The proper fee for this is a much larger sum, but the chemist will probably accept the offer and do all that is required.—H. Barnaby."

**Nickels's Improved Filtering-Funnel.**—In devising this new form of funnel Mr. Nickels has undoubtedly conferred a great boon on practical chemists, inasmuch as the time occupied in filtering is by its means very considerably reduced, thus facilitating what is very often a long and tedious operation. Some of the funnels are made so that they can be employed with a filter-pump. They also answer very well as an "Osmogene apparatus," all that is required being to fold the parchment paper in the form of a filter-paper, and to connect a piece of india-rubber tube and a stopcock to the outlet; the liquid to be dialysed is then poured into the inner funnel, and the outer jacket is filled with distilled water. As the water becomes charged with the products of diffusion it may be drawn off at frequent intervals, and replaced by a fresh supply, thus minimising the quantity of water necessary, a most important and essential condition of the operation.

## MEETINGS FOR THE WEEK.

Monday, 4th.—Medical, 8.30.
—— Royal Institution, 5. General Monthly Meeting.
Tuesday, 5th.—Institution of Civil Engineers, 8.
—— Pathological, 8.30.
Wednesday, 6th.—Geological, 8.
Thursday, 7th.—Chemical, 8. "Researches on the Constitution of Azo- and Diazo-Derivatives; Diazo-Compounds. Part II.," by R. Meldola, F.R.S., and F. W. Streatfeild.
—— Mathematical, 8.

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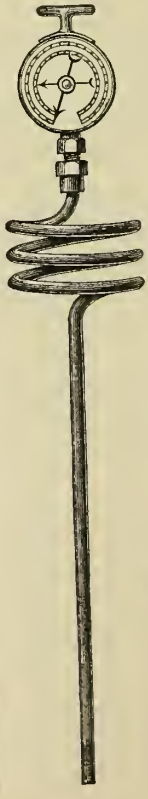

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THE CHEMICAL NEWS.

Vol. LV. No. 1428.

## ON COLOUR TESTS FOR STRYCHNINE AND OTHER ALKALOIDS.

By CHARLES L. BLOXAM.

The following characteristic and delicate test for identifying strychnine does not appear to have been noticed.

The alkaloid, on a glass slide or a porcelain crucible lid, is dissolved in a drop of dilute nitric acid, and gently heated; to the warm solution a very minute quantity of powdered potassium chlorate is added, which will produce an intense scarlet colour; one or two drops of ammonia will change this to a brownish colour, giving a brownish precipitate; the mixture is then evaporated to dryness, when it leaves a dark green residue, dissolved by a drop of water to a green solution, changed to orange-brown by potash, and becoming green again with nitric acid; these last changes of colour may be repeated any number of times.

The green colouring-matter is evidently a product of the action of ammonia upon the scarlet body, for if this be bleached by heating or by excess of chlorate, before the ammonia is added, the residue on evaporation is light brown, and yields with potash a bright yellow solution which is nearly bleached by nitric acid.

No other of the commonly occurring alkaloids which I have tried could be mistaken for strychnine by the above test, but each of them exhibits some peculiarity when treated in the same way, which would give a clue to its identity. This will be seen in the subjoined Table, in which the tests are supposed to be applied to the same portion of the alkaloid, as described above.

| | $HNO_3$. | | $KClO_3$. | $NH_3$. | Residue. | KHO. | $HNO_3$. |
|---|---|---|---|---|---|---|---|
| | Cold. | Heated. | | | | | |
| Strychnine .. .. | — | Pink. | Scarlet. | Brownish precipitate. | Green. | Orange. | Green. |
| Brucine .. .. .. | Violet; scarlet. | Yellow. | Yellow. | Bright yellow. | Green. | Dark brown. | Green; brown. |
| Narcotine .. .. | — | Bright yellow. | Yellow. | Dark brown. | Dark brown. | Dark brown. | Reddish yellow. |
| Morphine .. .. | Orange-red. | Yellow. | Yellow. | Red-brown. | Light brown. | Light brown. | Light brown. |
| Quinine .. .. .. | — | — | — | Green precipitate. | Light brown. | Light brown. | Light brown. |
| Cinchonine .. .. | — | — | — | White precipitate. | Light brown. | — | — |
| Caffeine .. .. .. | — | — | Pale yellow. | Bleached. | Red; yellow. | — | — |

Some few months ago I drew attention, in the Chemical News, to the use of bromine-water in the detection of alkaloids. I find that a more convenient reagent can be made by mixing a weak solution of potassium chlorate with enough strong hydrochloric acid to turn it bright yellow, and enough water to make it very pale yellow. This *euchlorine* solution is added by degrees to the solution of the alkaloid in HCl, which is boiled after each addition.

Strychnine gives a fine red colour, bleached by excess and returning when boiled.

Brucine gives a violet colour, in the cold, which is bleached by excess and restored by boiling.

Narcotine gives a bright yellow colour in the cold, which becomes pink on boiling and adding more of the euchlorine solution.

Quinine gives a faint yellowish pink on boiling.

After cooling the solution weak ammonia is gradually added.

Strychnine gives a yellow colour unchanged by boiling.

Brucine gives the same.

Narcotine gives a dingy green, becoming brown on boiling.

Quinine gives a bright green, becomining yellow on boiling.

Morphine gives no reaction; but if, after boiling with the euchlorine solution, the liquid be cooled and allowed to remain in contact with zinc for a minute or two, it will give the characteristic pink reaction with ammonia.

King's College, London,
March, 1887.

## RECENT RESEARCHES ON THE ACTION OF NITROGEN ON THE METALS IRON, COPPER, NICKEL, COBALT, &c.

By H. N. WARREN, Research Analyst.

The following is a description of the action of nitrogen on the more common metallic elements. The experiments being performed as follows:—Taking in the first instance the case of iron, finest merchant iron was selected in the form of puddled bars varying from a ¼ of an inch to 6 inches thick, and divided into lengths of about half a foot respectively, each piece being inserted in strong clay tubes or pipes, the one end being connected with an apparatus evolving pure dry ammonia gas. It was raised to a bright red heat by placing it horizontally across a charcoal furnace, the first sample being maintained thus during the passage of the ammonia gas for the space of two hours. Having been cooled in the ammoniacal atmosphere it was removed, and examined as to its properties both physically and chemically. The most striking physical properties were its intense whiteness of surface and its increased hardness, not admitting of being scratched so readily by means of a file. Its malleability was next determined by securing a bar of the same in a vice, leaving about half an inch projecting, and on applying a somewhat sharp blow it broke with a decided crystalline structure, exhibiting a fracture in all respects like that of siliconised steel. The bar was next submitted to longitudinal pressure, and broke under the hammer, or, in other words, split longitudinally, in so doing dividing into segments, and exhibited a somewhat malleable but at the same time a peculiar and highly crystalline structure; both determinations having been performed after cooling.

The bar was lastly submitted to careful analysis; qualitatively giving evidence of the presence of nitrogen through the formation of ammonia, this was quantitatively standardised by means of Nessler's reagent, the average of several results showing the sample to contain approximately about 0·004 per cent of nitrogen.

A second sample was submitted, under similar treatment, to four hours' action of the ammonia gas, and on the same tests being applied it proved to have increased twofold, both as regards its physical and chemical properties, breaking transversely with a fracture decidedly more crystalline and cleaving more readily longitudinally. The analytical determination of nitrogen was approximately 0·01 per cent.

Four similar bars were next treated, the action varying from six to twelve hours respectively; the last two were submitted to ten hours' action, and gave almost identical results with that of twelve hours, having become exceedingly brittle, breaking transversely on falling from a height of 6 feet, and containing upwards of 0·5 per cent of nitrogen.

A similar bar was next treated, being raised to a full white heat by means of a powerful fan machine, but gave identical results with respect to the percentage of nitrogen, &c. The experiment was next modified by substituting anhydrous protochloride of iron in place of the iron bar: volumes of ammonium chloride were at once evolved, and a silvery spongy mass of nitride of iron remained, containing upwards of 4 per cent of nitrogen. This, on being exposed to the atmosphere, in the course of a day or two became entirely converted into ferric oxide,—resembling the former specimens, though in a more marked degree.

These experiments were next varied by substituting copper bars for those of iron, the results being almost identical both in physical and chemical properties; presenting a highly crystalline surface, combined with a crystalline fracture and extreme brittleness, the percentage of nitrogen increasing according to the duration of the action. A somewhat peculiar phenomenon was observed on bringing several of these bars into the atmosphere before they were quite cold, several of the bars splitting transversely somewhat violently, they having apparently absorbed a quantity of the ammonia gas when at a high temperature and ejected it again on cooling; similar to the absorbing power of silver on oxygen.

An amorphous nitride of copper may be also formed as follows:—Pure dry cupric oxide, CuO, is introduced into a combustion-tube and connected with an apparatus for evolving dry ammonia gas; on the application of a gentle heat water is formed abundantly, and an amorphous green powder of copper nitride remains. Care must be taken so as not to allow of the tube becoming dull red, otherwise the nitride is decomposed with violence into metallic copper and nitrogen gas. An almost identical reaction takes place in the case of mercuric oxide when treated similarly, but in this case the heat must not be allowed to exceed 400° F., otherwise the nitride explodes with fearful violence, the compound resembling in all respects, as far as analytical results can be attained, ordinary fulminating mercury.

When chromium, nickel, cobalt, or manganous oxides were employed a corresponding nitride of the metal was obtained: it is, however, generally more advantageous in the case of chromium, &c., to use a chloride of the same. No such reaction, however, appears to take place when either the metal or the oxide of a metal—such as tin or stannic oxide, zinc or zincic oxide—are similarly treated. I have, however, formed small quantities of nitride of zinc by bringing zinc into solution by means of electro-dissolution, using an ammoniacal salt as a solvent. All the nitrides produced by these means apparently closely resemble one another with regard to their stability, resolving themselves into their component parts on the application of heat; their great brittleness also renders them absolutely unfit as commercial products.

## TITANIUM CARBIDE IN PIG-IRON.

By PORTER W. SHIMER, Easton, Pa.

On completing the filtration of a solution of pig-iron in hydrochloric acid, and after apparently everything had been transferred to the paper, a minute residue was observed remaining in the angle of the beaker in which the solution had been made. This residue had a steel-grey colour and metallic lustre, and was hard and gritty when touched with a glass rod. Placed under a microscope and magnified 400 diameters, the substance was found to be made up almost entirely of opaque cubical crystals with some fragments having the same colour and lustre as the cubes. The appearance was strikingly like that of a collection of crystals of iron pyrites.

The amount of material obtained—from 10 to 20 grms. of borings by solution in dilute hydrochloric acid, and careful decantation from graphite—was barely sufficient for a microscopic slide. A qualitative test of the minute amount of material obtained in this way showed the presence of considerable titanium. After many fruitless trials by decantation and other methods, sufficient material for quantitative analysis was finally obtained in the following manner:—

Two hundred and fifty grms. of the coarsest possible borings were dissolved in 7 litres of hydrochloric acid, of sp. gr. 1·03. A solution by the aid of heat took four to five hours. It was allowed to settle, and the clear solution poured off. Great care was taken that none of the material which had settled to the bottom was lost. The graphitic residue was then completely transferred upon fine bolting-cloth, previously stretched and fastened over the top of a beaker. All graphitic lumps were broken up by the finger while directing a strong stream of water from a wash-bottle upon it. When all but the larger graphite scales had passed through, the bolting-cloth was removed. This treatment separates the larger particles of graphite, which are troublesome in the subsequent separation, gives the particles more nearly a uniform size, and sets free many of the minute crystals which are to be separated. A magnet was then moved about in the liquid until all magnetic particles were removed. The material thus separated from the iron under experiment was found to be interesting, as will be shown further on.

The residue was allowed to settle into the angle of the beaker, and the liquid carefully poured off. It was then ready for the separation.

An inclined plane of window-glass, 12 feet long and 5 inches wide, was arranged in two sections, each 6 feet long, placed end to end. Narrow strips of glass, ½ inch wide, were cemented to the sides and upper end of each section. Each section was cemented firmly to a perfectly straight board about 6 inches shorter than the glass. These pieces, with the glass overlapping about 1 inch, were supported at a convenient height above a long table. For the present separation it was found that a fall of 1 inch in the first section and ½ inch in the second answered the purpose very well. A large beaker of distilled water, with syphon and stopcock, was placed at the head of the inclined plane, and water allowed to drop slowly upon it. By means of a camel's-hair brush the water was directed in a narrow stream, about 1 inch wide, throughout the whole length of the plane. Where the glass overlapped, a short glass rod was placed to lead the water to the lower section. At the end the water was led into a beaker by means of a long glass rod. The graphitic residue was then transferred to the head of the inclined plane with as little water as possible, and water allowed to drop slowly from the syphon.

The water at once begins to carry off the lighter and finer particles. It is necessary to keep tapping the residue with some convenient object, such as a platinum spatula, so as to prevent any graphite from being retained by the heavier crystals, and to keep the current flowing evenly over the whole residue. The separation soon becomes

apparent, the graphite being carried forward faster than the heavier crystals.

At this stage it is necessary to remove with a magnet any remaining magnetic particles, since these interfere with the separation. When, after three or four hours, all the graphite had been washed from the inclined plane, the water was drained off and the residue allowed to dry. When dry it formed a stream of bright metallic lustre throughout the whole length of the plane. The material was then swept together and treated in a beaker with hot hydrochloric acid, of sp. gr. 1·12, for the removal of a little iron. It was then again placed upon one of the sections of the inclined plane, and any remaining graphite separated from it. This second separation is not nearly so tedious as the first. Several separations of 250 grms. each were made, and about 1 grm. of pure material for analysis was obtained.

In the case of the iron under experiment it was necessary to have the borings as coarse as possible. In this way the scales of graphite are not so much broken up, and more can be separated by the bolting-cloth. The crystals also are less broken. When fine borings were used it was not possible to get a satisfactory separation on the inclined plane; for the small particles, instead of being independent of each other, as when coarse borings are used, gathered together in little clumps enclosing the crystals sought, which were thus carried off and lost.

The solution and separation should also be made on the same day; for when a solution is allowed to stand longer than necessary to settle there is a minute separation, perhaps of gelatinous silica, which interferes with the freedom of motion of the particles, causing them to gather in clumps, as described.

In the case of another pig-iron on which some preliminary experiments were made, the substance to be separated was still more finely divided than in the present case. It was here found best to give little, if any, fall to the plane, and to regulate the separation by means of the current of water. Successful separations were made with an inclined plane only 8 feet long.

A separation was also attempted upon a slowly revolving circular piece of glass 2 feet in diameter. The substance to be separated was placed in the centre of the glass and water dropped slowly upon it. It was thought that the water would carry the graphite to the periphery of the glass, leaving the heavier crystals in the centre. Only a little material could be separated in this way; but this result was plainly due to the fact that the glass used could not be made perfectly level. The great difference between the specific gravity of the crystals and graphite naturally suggests the usual separation by means of a dense solution; but the material is far too finely divided for successful separation by this means.

The material separated on the inclined plane, when deposited from water and dried, has a brilliant lustre and steel-grey colour. When swept together the mass has a deep iron-grey colour and little lustre. The lustre in the former case is due to the fact that, when allowed to deposit from water, the cubes arrange themselves unanimously with their faces upward, thus reflecting light uniformly.

On examining the material for analysis under the microscope, it was found to be free from graphite and to consist almost entirely of cubes, a large proportion of which were perfect. A few of the cubes had long handle-like projections from one of the angles. There were also occasional long, slightly tapering, nail-shaped crystals. The cubes varied in size from 1-1500th to 1-7000th of an inch (0·0169 to 0·0036 m.m.).

The material analysed has a specific gravity of 5·10. It is insoluble in hydrochloric acid, but readily soluble in nitric acid. The insolubility in hydrochloric acid explains how titanium in pig-iron is found and determined in the residue insoluble in this acid. The solubility in nitric acid shows how the titanium is eliminated in the nitric and sulphuric acid method for the determination of silicon in pig-iron. It is apparently wholly unattacked by a strong bolling solution of caustic potassa. When ignited for several hours, at a bright red heat, in a current of hydrogen, it suffers no change of weight. The following is the analysis:—

| | |
|---|---|
| Titanium | 71·58 |
| Carbon | 16·94 |
| Iron | 3·77 |
| Phosphorus | 0·69 |
| Manganese | 0·16 |
| Sulphur | 1·57 |
| Silicon | 0·00 |
| Nitrogen | 0·00 |
| Insoluble siliceous residue | 1·09 |
| Undetermined | 4·20 |
| | 100·00 |

The substance also contains a small undetermined amount of copper and vanadium, possibly in combination with sulphur. About 88 per cent of the material is thus seen to be a titanium carbide in which titanium and carbon are present in very nearly the exact proportion of their atomic weights. The formula is therefore TiC. In the calculation 48 was used as the atomic weight of titanium. The slight excess of titanium may easily exist in other combination. This compound is probably new, for I have not been able to find mention anywhere of any simple compound of titanium with carbon. The iron and phosphorus in the analysis are due to an admixture of the difficultly soluble phosphorus compound described below.

Determinations of titanium and carbon were made by various methods. In the first method dry chlorine gas was passed at a red heat over the substance contained in a weighed porcelain boat. The volatile chlorides were passed through numerous bottles and bulbs containing water. Titanic acid was separated from this solution and purified in the usual way. The carbon remaining in the boat was burned in a current of oxygen after first being freed from chlorine by passing hydrogen over it at a red heat. In another analysis the substance was burned directly in oxygen, the carbon thus determined agreeing closely with the first determination. The residue remaining in the boat was fused with potassium bisulphate, and the titanic acid separated in the usual manner.

I have found cubical crystals like those described in every one of five or six pig-irons that I have examined, one of them being a sample of English Bessemer pig-iron marked Barrow No. 1; but in none were they so free from admixture of the nail-shaped and other crystals as in the iron under experiment. This iron was a fine sample of No. 1 foundry iron, having the following composition:—

| | |
|---|---|
| Phosphorus | 0·343 |
| Silicon | 2·690 |
| Sulphur | 0·047 |
| Manganese | 0·594 |
| Titanium | 0·203 |
| Graphite | 3·664 |
| Combined carbon | 0·111 |
| Iron (by difference) | 92·348 |
| | 100·00 |

The titanium was determined in this iron by three different methods:—

1. The residue insoluble in dilute hydrochloric acid was fused with potassium bisulphate, and the titanic acid separated in the well-known manner. The result was 0·199 per cent titanium.

2. The residue insoluble in dilute hydrochloric acid was treated with nitric acid with the intention of dissolving out the titanium carbide,—a method suggested by this investigation. The nitric acid solution was precipitated by ammonia, the precipitate filtered, washed, and

re-dissolved in dilute sulphuric acid, and the solution boiled after neutralising excess of acid and adding sulphurous acid. The precipitate thus obtained was fused with sodium carbonate, extracted with water, and filtered. The insoluble sodium titanate was dissolved in sulphuric acid, and re-precipitated. The result was 0·206 per cent titanium.

3. Dry chlorine gas was passed over the borings at a red heat, and led through bottles and bulbs containing water. The result by this method was 0·205 per cent titanium.

It was found that in each of these three methods the first precipitates by boiling always contained phosphoric acid to such an extent as to cause very serious error when not separated. It was necessary, therefore, in each case to fuse the first precipitate with sodium carbonate and extract with water, thus separating soluble sodium phosphate from insoluble sodium titanate.

When properly carried out, the chlorine method certainly gives all the titanium in pig-iron. As much titanium was, however, found in the residue insoluble in hydrochloric acid by the first two methods as was found in the borings by the chlorine method. This proves that all the titanium, in this iron at least, is found in the residue insoluble in hydrochloric acid. It seems fair to conclude, then, that the titanium, instead of being uniformly dissolved in this iron, is mechanically disseminated through it in the form of a definite crystallised compound with carbon.

That part of the residue insoluble in dilute hydrochloric acid removed by the magnet was found to contain considerable phosphorus. It is not completely insoluble, even in very dilute hydrochloric acid, for on long boiling it dissolves. It is a finely divided granular substance, has a metallic lustre, and is so brittle that it may readily be ground to dust in a mortar. It encloses considerable titanium carbide. Samples separated at different times contained phosphorus as follows:—10·32, 12·50, and 11·90 per cent. These varying results are due to varying conditions of time, temperature, and strength of acid. One of the samples contained 69·48 per cent of metallic iron. When only slightly heated, apparently not much above the boiling-point of water, partial oxidation takes place, a bright glow spreading over the whole mass. On further heating the substance fuses easily. The compound appears to be completely insoluble in double chloride of copper and ammonium.

Duplicate determinations of the phosphorus remaining insoluble in a solution of the double chloride gave 0·155 and 0·158 per cent phosphorus. That is, 45·63 per cent of the total phosphorus in this iron remains in the insoluble residue in the form of a high-phosphorus compound!

From the residue insoluble in dilute hydrochloric acid only about 12 per cent of the total phosphorus could be separated by means of a magnet. I have not yet attempted a separation on the inclined plane of the residue insoluble in double chloride solution.

These notes on the phosphorus compound are only preliminary, for, owing to want of sufficient material, I have not been able to make a complete investigation of it.

I have great pleasure in acknowledging my indebtedness to Mr. Frank Firmstone, of the Glendon Iron Works, who not only gave me the facilities of a large iron works, but greatly encouraged me by his interest in the progress of this investigation.

**Determination of Uric Acid by Means of Potassium Permanganate.**—Ch. Blarez and G. Denigés.—The conditions necessary to be observed in determining uric acid by permanganate are as follows. The minimum dilution should be 1 part in 8000. The quantity of uric acid operated upon should not, if possible, exceed 0·1 grm. The quantity of free sulphuric acid should be about 3·5 grm.—*Comptes Rendus*, Vol. civ., No. 11.

ON THE

# PHYSICAL PROPERTIES OF MANGANESE STEEL.*

By W. F. BARRETT

Professor of Experimental Physics in the Royal College of Science for Ireland.

At the British Association meeting in Aberdeen, in 1885, Mr. J. T. Bottomley read a brief note on "A Specimen of Almost Unmagnetisable Steel." As the magnetisation of iron was a subject on which I had worked for some time, Mr. Bottomley was good enough to hand over to me this remarkable specimen of steel for further investigation, at the same time giving me the name and address of Messrs. Hadfield and Co., Steel Founders, of Sheffield, the patentees and manufacturers of this steel.

Upon writing to Messrs. Hadfield, they furnished me with the result of a chemical analysis of their patent steel, which is as follows:—

| Fe. | Mn. | C. | Si. | P. | S. |
|---|---|---|---|---|---|
| 86·68 | 12·25 | 0·80 | 0·15 | 0·10 | 0·02 per cent. |

Other varieties of this steel are manufactured, but this is the most generally serviceable. Specimens of this steel were first exhibited at the Institute of Mechanical Engineers in London in the early part of 1884, and a paper describing this material appeared in the *Engineer* for February 8, 1884. From this paper I make the following quotation:—

"It is sufficiently well known that manganese has been employed for many years in the manufacture of steel in various proportions, but anything exceeding 1 per cent, it has been generally believed, would render the metal under treatment worthless, and any further addition thereof in excess of this proportion has been considered impracticable. In fact, Dr. Siemens had stated publicly, on many occasions, that the use of manganese was simply a cloak to cover the impurities in steel making, that it covered a multitude of sins: and this was the general opinion of the steel trade. Messrs. Hadfield, of Sheffield, however, engaged in a long series of experiments and tests, with the object of discovering its truth, and after a considerable expenditure of time and capital, discovered that by adding the ordinary ferro-manganese of commerce to iron or steel in such proportions as to produce in the steel or decarbonised iron under treatment a percentage of manganese varying from 7 to 20 per cent, that the most beneficial results could be obtained. Such percentage is regulated according to the purpose for which the steel is required. For instance, to produce a steel suitable for armour-plates and other purposes, as we mentioned last week, they add about 10 per cent of rich ferro-manganese, containing, say, 80 per cent of manganese, thus obtaining a steel containing about 10 per cent of manganese. For railway purposes they add about 11 per cent, for steel toys and tools about 12 per cent. They pour this ferro-manganese into the molten steel under treatment, thoroughly incorporating it therewith, and then run it into ingot or other suitable moulds, and allow it to cool, after which it is ready for use, as it requires neither tempering, rolling, forging, nor hardening. This treatment of steel in suitable proportions, according to requirements, appears to be novel, and renders the steel so manufactured harder, stronger, denser, and tougher than most steel now manufactured, even when forged and rolled. This steel may, however, be forged and rolled in the ordinary manner. *For casting* it has the advantage that it possesses greater freedom from honeycombs and similar defects; but the most peculiar property is its great toughness, combined with extreme hardness. It is through this that the hitherto indispensable processes of rolling, forging, hammering, hardening, and tempering may be dispensed with, thus effecting for many articles an enormous economy in time, labour, and expense. In casting its fluidity enables fine steel castings to be made

* A Paper read before the Royal Dublin Society, December 15, 1886

without misrunning, and approaching in smoothness iron castings.

"Amongst the samples of the steel placed on the table at the meeting of the Mechanical Engineers was a sample test bar containing 12 per cent manganese, bent double when cold, though hard enough for turning iron; a sample from same ingot shows a tensile strength of 42 tons per square inch, with 20·85 per cent elongation; several hammered pieces; a manganese adze, containing 20 per cent manganese, just as it left the mould; an axe, containing 12 per cent manganese, just as cast in the rough, had chopped through ½in. square iron. This, like the others, had not been hardened or tempered, only the edge ground."

In a paper read before the American Institute of Mining Engineers in May, 1884, some tests of this steel were given, showing the extraordinary tenacity and hardness of the material. When hammered or drawn into rods it loses some of its toughness, and becomes exceedingly hard.

If now the steel be heated to a yellow or nearly welding heat, and then suddenly quenched in cold water, instead of becoming harder it loses some of its hardness, and becomes exceedingly tough, so that the effect produced upon manganese steel is just the opposite to that produced upon ordinary steel, which is of course rendered hard and brittle by sudden cooling.

It was important for the purpose of my investigation to obtain a specimen of manganese steel drawn into wire, and Messrs. Hadfield endeavoured to draw some for me. In this they did not at first succeed; so I begged Messrs. Rylands, of Warrington, whose extensive wire-drawing works are well known, to make the attempt. They were good enough to oblige me, and, after several ineffectual trials, wrote :—"We gave the steel into the hands of our most experienced wire-drawer, a man who is accustomed to draw crucible steel wire; but he says that although he gave it every facility, putting only half a size on to it, the steel will not draw at all." After much time had been lost in these attempts, Messrs. Hadfield, at my request, once more undertook the task themselves; and I am glad to say they have now been completely successful. The specimens here exhibited for the first time are long lengths of manganese steel wire, No. 13 S.W.G., and also No. 19 S.W.G., of two kinds, hard and soft. I requested Messrs. Hadfield to let me know the method of wire-drawing they found successful, and the following is their account of the process adopted in drawing manganese steel into wire :—

"When first trying to reduce this material from the rolled rods into wire, it was attempted to draw it straight away from the rods; but, owing to its hardness, very little progress could be made, as the wire kept breaking in short lengths. Several methods were tried, such as softening it by annealing, as in ordinary wire; but this seemed to make very little difference.

"As exceedingly good bending tests had been obtained with bars of the same steel when heated to a yellow heat, and plunged into cold water, it was thought worth while attempting a similar experiment with the rolled rods before trying to draw it down into wire. The rods were coiled up, heated to a yellow heat over a smith's fire, and then plunged into cold water. It was then easily drawn into wire, starting with No. 7 gauge, when it was drawn to No. 9 with safety. This drawing again took out the requisite ductility, and it was therefore necessary to again heat the wire, and plunge it in the same manner as before. By doing this each time the wire was reduced two numbers of the gauge; there was no difficulty whatever in drawing it to any desired fineness, the only point necessary being that the wire must be heated sufficiently hot before plunging into cold water, or the wire would be still too hard. The colder the water the better the result."

The composition of the manganese steel from which the wire was drawn is slightly different from the specimen I obtained from Mr. Bottomley. The analysis of the wire is as follows :—

| Iron. | Manganese. | Carbon. | Silicon. | Phos. | Sulphur. |
|---|---|---|---|---|---|
| 84·96 | 13·75 | 0·85 | 0·25 | 0·10 | 0·09 p.c. |

I have now to lay before the Society the results of some of my experiments with this material:—

*Density*.—The density of the manganese steel wire I find is 7·81, that of ordinary steel being 7·717.

*Hardness*.—In its ordinary condition manganese steel is very hard. It easily scratches steel that is not hard-tempered.

*Modulus of Elasticity*.—The modulus of elasticity (Young's Modulus) was determined by direct stretching. Experiments were made with the ordinary hard manganese steel wire and with the same wire annealed by sudden cooling. A length of four metres was suspended from a well-constructed clamp of a new form, devised and made for me by Messrs. Booth Brothers, of Dublin, and the readings were taken by an excellent cathetometer. The flexure of the support under the maximum stress was carefully tested and found to be inappreciable. An initial weight of 2000 grammes was kept on the wire, and additions were made of 10,000 up to 40,000 grammes; with the maximun weight there was no set, the index accurately returning to zero when the weights were removed. Three elongations were made in each of five sets of observations, the mean of the fifteen trials giving a modulus of 16,800 *kilogrammes per square millimetre*. Another set of observations were made with an initial stress of 5000 grammes; adding to this 38 kilogrammes, on and off, the mean of three sets of observations thus made gave a rather higher number, namely, 17,130 kilogrammes per square millimetre.

Mr. M'Cowan, B.Sc., the Demonstrator in Physics at the College of Science, also took a set of careful observations; the number he independently obtained was somewhat lower, namely, 16,470 kilogrammes per square millimetre.

The mean of these three series of experiments is the same number as the mean of the first fifteen experiments, viz. :—

16,800 kilogrammes per square millimetre,

or $1680 \times 10^6$ grammes per square centimetre, which may be taken as the modulus of *hard manganese steel wire*. The diameter of the wire used was 0·98 millimetre, and the length under observation 3·455 metres,

The *soft* manganese wire was now tried. Six sets of experiments were made with three or four elongations in each, the mean of twenty elongations giving a modulus of

16,710 kilogrammes per square millimetre,

slightly below that of the hard wire.

These numbers are lower than I expected. Iron has a modulus of 18,610 kilos. per square millimetre. Steel wire varies from 18,810 up to pianoforte wire, which is 20,490 kilogrammes per square millimetre.

But this comparatively high rate of extensibility of manganese steel is for many purposes a considerable advantage, as it enables the material to give under a sudden stress without fracture.

(To be continued).

# PROCEEDINGS OF SOCIETIES.

## THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

*Annual General Meeting, March* 14, 1887.

### Address of the President, Dr. Odling, M.A., M.B., F.R.S., &c.

By the provisions of the Royal Charter under which the Institute of Chemistry was incorporated on the last day of June, 1885, it was required among other things that the Institute should with all reasonable expedition, by resolution of a General Meeting, make bye-laws for regulating

the conduct of the affairs and property of the corporation; that the bye-laws so made by the Institute should not have effect until they had been submitted to and allowed by the Lords of Her Majesty's Privy Council; and that until the bye-laws had been so allowed, the affairs of the corporation should be conducted by the first appointed Council of the Institute in accordance with the Articles of Association of the original Institute founded in October, 1877, so far as they were not inconsistent with any express provision of the Charter. As regards the provision of the Charter declaring that the bye-laws of the Institute should not have effect until they had been allowed by the Lords of the Privy Council, I have the satisfaction of being able to inform you that these bye laws, as made by resolution of a General Meeting held on February 4th, 1887, confirmed at a subsequent General Meeting held on Feb. 15th, 1887, received, so lately as February 24th of the present year, the formal allowance of the Privy Council; so that for the last fortnight, the conduct of the affairs of the Institute has had to be, and henceforward will have to be, in accordance with the bye-laws of the Institute, now made and allowed as required by the Charter.

The bye-laws of the Institute, thus given effect to, are in the main identical with those first made at a General Meeting of the Institute held so far back as March 26th, 1886; and are based, as nearly as might be, on the Articles of Association of the original Institute. At different intervals since March 26th, three separate sets of suggestions and requirements have been put forward by the Privy Council; and though the successive consideration of these has had the disadvantageous effect of taking up a good deal of time, it must frankly be admitted that the careful criticism to which the bye-laws, as first made, have been subjected by the Privy Council, has resulted in their greater consistency and better fitness for their intended use. The final insistance by the Privy Council on one or two slight verbal alterations has caused indeed some little extra delay; but on most points their representations and requirements could not but be recognised at once as advantageous and called for; while on other points our counter-representations were eventually acceded to by them in a spirit of consideration and reasonableness demanding our thankful and hearty acknowledgment.

The bye-laws first submitted to the Privy Council, namely, those made on March 26th of last year, dealt with a proportion of the originally appointed Officers and Council of the Institute as ineligible for re-appointment by election of the Fellows, at the first General Meeting to be held under the bye-laws. It was pointed out, however, that this proposed ineligibility was contrary to the provisions of the Charter, which expressly declared the eligibility of the whole of the originally appointed Officers and Council for re-appointment by election. Thus it is that the Officers and Members of Council now holding office, together with three other Fellows of the Institute who have been most largely approved as suitable to fill the vacancies which have occurred, present themselves for election at this the first election held under the Charter and bye-laws. At every subsequent Annual General Meeting and election, however, one-third of the Vice-Presidents and Members of Council will, as heretofore under the articles of association, be ineligible for re-appointment. It being required by the bye-laws that the holding of the election and Annual General Meeting should be on the 1st of March, or on some day between the 1st and the 15th of March, the meeting has, on this occasion, been put off until the latest included date. For the announcement of the meeting having to be made before the bye-laws had been formally allowed by the Privy Council, it was thought desirable to afford the longest possible opportunity for their being so allowed before the time of holding the meeting; since in default of their being so allowed, the election of Officers and Council, which according to the provisions of the Charter can only be held under the bye-laws, and consequently not until after their allowance, could not have been held at the meeting at all, and must indeed have been postponed for another year. In future, however, it will probably be desirable to hold the Annual General Meeting and election as soon as may be after the 1st of March.

Under the provisions jointly by the Charter and the bye-laws, the Council of the Institute has entrusted to it no inconsiderable powers. It constitutes, however, but the chosen executive of the entire corporate body, who are indeed the body responsible alike for the general policy of the Institute, and the regulation, broadly, of its affairs. The desirable continuity in any course of action pursued by the Council is provided for by the circumstance of two-thirds of its members being eligible for re-appointment at each successive Annual General Meeting. The desirable renovation of the Council, and its continuance in touch with the general body is provided for by the circumstance of the whole of its members vacating office every year; by one-third of the old members being ineligible for re-appointment; and by the official nomination of one-third of the new members being left in the hands of the general body. The powers of the Council are, moreover, limited by the conditions that they are to be exercised in accordance with, and subject to the provisions of the Charter and bye-laws of the Institute; that they are to be subject also to the control and regulation of any General Meeting; and that they are not to be exercised in respect of certain matters—such as the making of bye-laws and the purchasing or erecting of any building—which, under the provisions of the Charter, require to have the sanction of a General Meeting. Doubtless, it must and will happen from time to time that the action of the Council, determined on after consideration and discussion, of representations and counter-representations brought specially under their notice, may not have the approval of individual Fellows; but it will clearly be the fault of the general body, if the general course of action of the Council, subject as it is in so many ways to their direction, is not in accordance with their prevailing wishes.

It should be fully understood that the Institute of Chemistry is essentially a professional organisation, having in view professional objects. Its primary function is not the dissemination of scientific knowledge, but the assurance of scientific attainment. It is, indeed, the organisation of a highly scientific profession; probably the most, certainly one of the most, scientific of all existing professions. And its chief purpose is to ensure and improve the scientific training of those practising the profession, by setting up a high standard of scientific proficiency, and by certifying to the attainment of such a standard on the part of its registered members. As regards persons already in practice, its attestation must necessarily be based on the evidence available that they have, for not a few years, practised their profession with approved skilfulness and good repute. Such persons may well be depended on to maintain the character of the profession, and to justify the attestation accorded them. But it is with the future of the profession, as determined by the training and character of those entering its ranks, that the Institute is chiefly concerned. The gradual elevation and advancement of the profession in general, on the one hand by the educational and other demands made on every one admitted into the corporation, and on the other hand by the inducement which admission to membership of the corporation will hold out to educated men, is the declared purpose for which the Institute was originally founded,—a purpose spoken of in the Royal Charter, under which it has since been incorporated, as "laudable and deserving of encouragement." Accordingly, in the case of all persons now entering the profession, not only are they required to show a practical familiarity with chemical operations as tested by the Institute itself, but they have in addition to furnish satisfactory evidence alike of general scientific training and general scientific attainment.

The Institute of Chemistry having been successively founded and incorporated with a view to the organisation and elevation of the chemical profession, it is

to the achievement of this object that its efforts are properly directed; and it is by the more or less full achievement of this object that it must eventually claim to be judged. Despite many difficulties, owing in the first instance to the unsuitability of its constitution to the purposes and influences it aimed at effecting, and latterly to the transitional stage through which it has passed, it has admittedly achieved no inconsiderable amount of success. From this time forward, favoured by its Royal Charter, and acting now for the first time under its own bye-laws, it starts anew on its career, with a smoother course and more hopeful prospects than ever yet lay open before it. It prefers a claim upon all engaged in the profession of chemistry to interest themselves in its welfare, and to make its now completed organisation serviceable to good ends, and a means of advancing the profession to which they are attached, and of which they feel so justifiable a pride in being accounted members.

Unfortunately, the objects which the Institute of Chemistry is intended to subserve are not such as afford occasion for frequent personal intercourse, or for the circulation of beneficial printed communications among its Fellows,—means which habitually exert so large an influence in binding members of one and the same corporation to one another, and sustaining their interest in the corporation to which they in common belong. Requirements of education, examination, attestation, and registration are not matters habitually calling forth a strong enthusiasm of grateful recollection. But in default of any such enthusiasm, the Institute, especially in the still early stages of its career, prefers a claim on its members for steady continuous accord and support. While carefully guarding the portals of the profession, it further aspires to safeguard the interests of those admitted within the precincts. It is now to a considerable extent, it looks forward to being to a far greater extent, the means of assuring to the carefully trained and honourably conducted professional chemist a recognised claim and position against which the unqualified and meretricious will feel it in vain to contend. Strongly desiderated, as it has been by many of the younger and more earnest of the profession, it appeals to the good-will and fostering interest of all; and of those, more especially, whose already assured position puts them personally beyond the scope and influence of its looked for usefulness and future success.

But the possession of adequate scientific qualification to enter a profession is one thing, the maintenance of high scientific qualification to practise the profession is another. The first named qualification, as the result of a special prescribed study, can alone be tested and attested by the Institute; the last named qualification is necessarily dependent on a voluntary perseverance in scientific study and a maintained interest in scientific progress. The advances of scientific chemistry are nowadays so rapid, and the development of applied chemistry follows so closely on the heels of scientific discovery, while pointing the way to yet further discovery, that the professional chemist, more, perhaps than any other professional man, is placed in the happy position of being bound, throughout his life, to continue a student of science, and a contributor, in one way or another, to its advancement. A student, if only for his own sake, he must be; a teacher he may be, and on many grounds it is desirable that, in some cases, he should be. With but few exceptions, some of them it is true very eminent exceptions, the leading chemists of the country are the holders of professorial positions; and would it be other than a loss to professional chemistry, and to the many great interests committed to the care and judgment of professional chemists, if practitioners and professors were to be, from the first and throughout, broadly marked off from one another? Would it, for example, be for the public advantage that Professor Williamson, Professor Frankland, Professor Roscoe, Professor Tyndall, Professor Dewar, and others, should be debarred from affording their professional services to the Board of Trade, to Royal Commissions, to the Judicature, to the Trinity House, to the Home Office, to the Board of Works, to the Board of Inland Revenue, and to other municipal or state departments? Would it again be for the public advantage that the chemists exclusively engaged in these and other departments should, in particular cases of difficulty and doubtfulness, be unable to have the professional cooperation of their professorial brethren; that the men eminent for highly specialised knowledge should, in their responsible positions, be refused, from time to time, the desired cooperation of men with a different and wider range of knowledge? Would it be for the advantage of the many large interests confided to them that the body of professional chemists throughout the land should be a body wholly apart from and not amenable to the influence of association, on an equal footing with the holders of professorial positions and recognised leaders of chemical thought in the country?

On the other hand, the gain to professorial teaching and even to investigation, from the occasional engagements of the professoriate in various branches of professional work, would seem not to admit of question. Technical chemistry is the necessary and friendly illustrative of general chemistry; and such a knowledge of technical chemistry as is only to be acquired by the responsible conduct, from time to time, of technical inquiries, is by no means the least essential item of knowledge demanded in professorial teaching. General chemistry, while distinct from technical chemistry properly so-called, has this in common with it, that it comprises a study of all the more important chemical changes taking place or effected, on a large scale, in the different processes of nature and art. It is necessary for the student to complete his chemical education by being made acquainted with these different changes and processes viewed as chemical phenomena; since by their study he is enabled to acquired a far better understanding of the nature and results of chemical change than he could possibly get by a study of laboratory processes only, conducted mostly on a small scale and with a different object. The teaching of scientific chemistry is not meant only or chiefly for those of independent means, who throughout their lives are to be exclusively students and inquirers; but is meant in large measure for those who, in some way or other, are to make their study of the principles of chemistry available for their own needs, and directly contributory to the prosperity and productiveness of the country. It is for the professor of chemistry, by that familiarity with technical operations which is attainable only by occasional participation in them and responsibility with regard to them, to make himself qualified to direct the pupil in his scientific study of technical processes, considered as among the largest and most important illustrations of chemical change. In many ways, indeed, it is for the advantage of those whom he teaches that he should not hold himself aloof from the professional pursuits for which the majority of them are qualifying themselves under his instruction and guidance. The question is not between a teacher fulfilling the special duties of his chair assiduously and earnestly, or perfunctorily and indolently; for among not the least active and renowned of teachers have been found those largely engaged, from time to time and in one way or other, in professional work. But the question is, assuming the attention of the teacher to be available in some measure for other duties, whether his duly paid for occasional engagement in the work of technical enquiry is not, at least, as cognate and professorially improving as his alike paid for, more or less continuous engagement in the not over edifying work of examinership, secretaryship, directorship, editorship, hack-authorship, and so forth. To be engaged in the profession of surgery, of medicine, of law, of engineering, and of fine-art, &c., is an almost essential requirement of the professor of each of these subjects; and to be engaged in the profession of chemistry cannot, it would seem, be otherwise regarded than as a valuable contributory qualification of the professor of chemistry. In support of this position, I would invite your attention

to the substance of a letter communicated, some time back, by Professor Frankland, to the Chemical News.* As this letter was called forth by way of reply to an elsewhere-appearing alike foolish and rancorous attack on the Institute, to which it is not worth while to accord the importance of more than a passing mention, I have persuaded Professor Frankland here and there to alter the wording of his letter, excluding from it, as far as could be, all animadversion on the little ebullition of editorial pique, to which it was only too serious a rejoinder. For editors, even professor editors, "however they have writ the style of gods," have yet their besetting frailties; tall-talking, rather than plain-dealing, being, indeed, their too delightful privilege, and ever fondly resorted to weapon, serving them both as sword and shield.

In common with other great gifts, the power of making important contributions to knowledge and doctrine is, in its very nature, a rare power. Whatever his desires, opportunities, and efforts, it is not given to everyone to be a great discoverer. But to every member of a scientific profession it is given to do good and useful work in science, and in the applications of science. More especially it is incumbent on the professional chemist to be not unmindful of, nor is he found to be unmindful of, the special opportunities afforded him. By his function and training he would seem to be of necessity an investigator; since to analyse necessarily implies to investigate. Always, indeed, should it be borne in mind that the varied work of the professional chemist, in its different degrees of magnitude, responsibility, and originality, is essentially scientific work, claiming to be conducted in a scientific spirit. As but few among us can be in, or near, the first rank of discoverers, so neither can many of us be holders of the first professional positions, and doers of the most dignified and highly remunerated professional work. But as it is for the youthful, the little heard of, and the struggling worker to pride himself on belonging to a definite learned profession, including in its ranks the most eminent and revered of his masters in science, so it is for everyone, no matter how high his position, who is, or has been, engaged in any way in professional chemistry, and takes interest in the professional career of his pupils and successors, to recognise the tie which binds him and his fellow workers together. It is for all alike to acknowledge a mutual claim on each other's consideration and good will, and a common obligation to the now organised profession of which all alike are members.

## PHYSICAL SOCIETY.

*March 26th, 1887.*

Prof. Balfour Stewart, President, in the Chair.

Mr. Edmund van Aubel was elected a member of the Society.

The following paper was read:—

"*On the Production, Preparation, and Properties of the Finest Fibres.*" By Mr. C. V. Boys, M.A.

The enquiry into the production and properties of fibres was suggested by the experiments of Messrs. Gibson and Gregory on the "Tenacity of Spun Glass," described before the Society on Feb. 12, and the necessity of using such fibres in experiments on which Prof. Rücker and the author are engaged.

The various methods of producing organic fibres, such as silk, cobweb, &c., and the mineral fibres, volcanic glass, slag wool, and spun glass, were referred to, and experiments shown in which masses of fibres of sealing-wax or Canada balsam were produced by electrifying the melted substance.

In producing very fine glass fibres, the author finds it best to use very small quantities at high temperatures, and the velocity of separation should be as great as possible. The oxyhydrogen jet is used to attain the high temperature, and several methods of obtaining a great velocity have been devised. The best results obtained are given by a cross-bow and straw arrow, to the tail of which a thin rod of the substance to be drawn is cemented. Pine is used for the bow, because the ratio of its elasticity to its density (on which the velocity attainable depends) is great. The free end of the rod is held between the fingers, and when the middle part has been heated to the required temperature the string of the cross-bow is suddenly released, thus projecting the arrow with great velocity and drawing out a long fine fibre. By this means fibres of glass less than 1-10,000th of an inch in diameter can be made.

The author has also experimented on many minerals, such as quartz, sapphire, ruby, garnet, felspar, fluor-spar, augite, emerald, &c., with more or less success. Ruby, sapphire, and fluor-spar cannot well be drawn into fibres by this process, but quartz, augite, and felspar give very satisfactory results. Garnet, when treated at low temperatures, yields fibres exhibiting the most beautiful colours.

Some very interesting results have been obtained with quartz, from which fibres less than 1-100,000 of an inch in diameter have been obtained. It cannot be drawn directly from the crystal, but has to be slowly heated, fused, and cast in a thin rod, which rod is attached to the arrow as previously described.

Quartz fibre exhibits remarkable properties, as it seems to be free from torsional fatigue, so evident in glass and metallic fibres, and on this account is most valuable for instruments requiring torsional control. The tenacity of such fibres is about 50 tons on the square inch.

In the experiments on the fatigue of fibres great difficulty was experienced in obtaining a cement magnetically neutral, and sealing-wax was found the most suitable.

An experiment was performed illustrating the fatigue of glass fibres under torsion, and diagrams exhibited showing that the effect of annealing them is to reduce the subpermanent deformation to about 1-10th its original amount under similar conditions.

Annealing quartz fibres does not improve their torsional properties and renders them rotten.

Besides the use of quartz for torsional measurements, the author believes that quartz thermometers would be free from the change of zero, so annoying in glass ones. He exhibited an annealed glass spiral capable of weighing a millionth of a grain fairly accurately, and also a diffraction grating made by placing the fine fibres side by side in the threads of fine screws. Gratings so made give banded spectra of white light.

The author regretted that his paper was so incomplete, but thought the results already obtained would be of interest to the Society.

Prof. W. G. Adams congratulated the author on his most interesting paper, and considered the results to be of great importance. He believed the banded spectra exhibited by the grating were probably due to internal reflection within the fibres.

Mr. Cunyngham asked whether the glass mirror used in the torsional experiments was magnetic, to which the author replied that this was probable, but even this assumption did not explain all the peculiarities observed.

A paper by Prof. Pickering was postponed till the next meeting, on April 23rd.

* Chemical News, Dec. 18, 1885 vol. lii., p. 305.

Nitrogenous Derivatives of Turpentine.—C. Tanret.—The author has isolated two isomeric compounds having the composition $C_{20}H_{17}NO_4$. The compound $\alpha$ melts at 210° and boils at 283° with partial decomposition; $\beta$ begins to melt at 100° and boils at 274°. Their characteristic reaction is the fine violet colour which a trace of these bodies gives with ferric salts.—*Comptes Rendus*, Vol. civ., No. 11.

## NOTICES OF BOOKS.

*The A B C of Modern (Dry Plate) Photography.* By the London Stereoscopic Company, Limited. London. 1887. (Twenty-second Edition.)

The previous editions of the "A B C of Modern Photography" having been so successful, the publishers have, in issuing the 22nd edition, taken the opportunity of enlarging it by one hundred pages, and adding to the work much fresh matter which recent advances in the science have rendered desirable, if not necessary; in fact this latest edition may almost be considered to be a new book.

Part I., beginning with the choice of apparatus, gives a list of all the apparatus necessary for taking a picture, and, after commenting shortly on the time of exposure, development and fixing are thoroughly explained; in fact this, the first part of the handbook, is devoted entirely to the manipulative part of photography.

Part II. is for advanced students, and it is recommended that the reader should master the first part before attempting to go on any farther in the work. It commences with a few remarks on lenses, and points out the differences between lenses for portraits and those for landscapes, &c. Amateur portraiture is, however, generally unsatisfactory, principally on account of the operator not having a properly fitted-up studio, with all the indispensable appliances for arranging and controlling the light and shade. It seems, therefore, hardly necessary to do more than lightly touch on the subject in a book of this class, intended specially for beginners.

The chapters on photo-micrography (or, as we should prefer calling this art, micro-photography) and instantaneous photography are both interesting and instructive. Several shutters are described and illustrated, and their respective merits or demerits pointed out. The advantages of using paper negatives are next dwelt upon, not the least of which is the diminution of weight to be carried about; another is the absence of what is known as "halation," or the effects of reflection from the back surface of the glass. New apparatus and processes are finally given: the new method of printing known as the "platinotype process" is fully explained; the advantage of this process is that the pictures obtained will not fade, but are as permanent as the paper itself. Another comparatively new method of printing is the "carbon" process—a modification of which is known as the Woodbury type, by which means hundreds of copies can be reproduced at a low price.

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*Report of the Assistant-Chemist to the New York Agricultural Experiment Station.* By E. F. Ladd. Elmira, N.Y. 1887.

During the past year Mr. Ladd has, besides the routine work of the Station, continued his examination of feeding stuffs in respect to their chemical composition and digestibility. A process of saponification promised well for measuring the digestible fat in coarse fodders, but the difficulty of filtering prevented its use with meal and similar products.

The processes used in the digestion of the albumenoids are the same as given in the last report, except that 1 grm. of the substance is always used, as it can be worked to better advantage. In order to test what effect each part of the digestive fluid has, a few experiments were made with different quantities of the fluid, and the results are given in a table: when a small quantity of starch or sugar is added, the amount digested is diminished in proportion.

In artificial digestion trials it is usual to continue the operation, after the digestion with gastric juice, by means of a pancreatin solution; but Mr. Ladd's experience with the pepsin method has failed to give such uniform or high results, on the whole, as when the pancreatin digestion was omitted. To find the degree of fineness for the best digestion a sample of corn was divided into three parts—one coarse, another fine, and the third between the two; a difference of 20 per cent was found in favour of the fine over the coarse. In a previous report Mr. Ladd has called attention to the subject of heated corn-meal, and investigations by Husemann and others have shown that such meals frequently contain a toxic principle belonging to the class of ptomaines, due to putrid decomposition of the nitrogenous portions of the corn-meal. He has now succeeded in isolating a small quantity of this poison from a sample of badly heated meal; when slowly evaporated from an ethereal solution it gave urea-like crystals. The quantity as yet obtained is not sufficient to make a proper study of the physiological effects, but the author will carry this out at the first opportunity. The ill effects sometimes arising from feeding on cotton-seed meal he suspects may be due to similar causes, but he has not yet attempted to see whether ptomaines are present or not in such cases.

Ptomaines are not confined to the food of our domestic animals, but have been found in many substances used for the food of man. When decomposition is allowed to set in before being used, serious cases of poisoning have been known to result from eating cheese and milk which were really unfit for use.

A table is given of the analyses of eighty-four grasses, hays, grains, &c., and it is noticeable that the percentage of albumenoids in the grasses are rather lower on the whole than is generally thought. This may be due to the sampling, which was done by Mr. Ladd himself, and may be considered to be as fair a sample as could be taken.

Table II. gives the results of the experiments on digestibility of the same foods; the clovers are found to be the richest in albumenoids of any of the hays, and a larger percentage is digestible. Buttercups are richer in albumenoids than daisies, and are nearly twice as digestible; but the most highly nitrogenous food of anything yet analysed is the *Soja hispida* bean, the crude albumenoids being 43·75 per cent, of which the digestive coefficient was 95·32 per cent.

Probably in no other determination in fodder analysis is there likely to be so wide a variation in the results obtained by different chemists as in the fibre: this is chiefly due to the different methods used and the temperatures employed in the determination.

Mr. Ladd gives five different methods which can be and are used in different laboratories, and the results are analysed in several tables.

The work Mr. Ladd is engaged upon will be found to be of great value to stock raisers, besides being of interest to chemists and physiologists.

## CORRESPONDENCE.

### TRANSPARENCY OF MOLTEN METALS.

*To the Editor of the Chemical News.*

Sir,—A letter appeared in your journal some weeks ago concerning the alleged transparency of molten cast-iron, and I have looked for several weeks hoping to see the statement of Dr. Ramsay either confirmed or contradicted. I would not desire to rashly contradict a statement made by one who has so many claims to be considered an accurate observer as is the case with Dr. Ramsay, but at the same time I think the alleged transparency should not be accepted as a fact without further evidence. That many metals, when at a high temperature, appear clear and transparent is well known, and as examples it is only necessary to mention silver or gold in cupellation, or copper during refining. But despite this clear bright appearance these metals are still opaque, for it is not possible to see the bottom of the cupel or

crucible through even a very thin layer of metal. If cast-iron really is transparent, it would certainly be contrary to my conceptions not only of the characters of iron itself, but also of the 10 per cent, or so, of other elements—such as carbon and silicon—which exist, probably in a state of solution, in the iron.

I have often had an opportunity of seeing tons of iron and steel poured, and never remember to have seen anything corresponding to transparency. It is not possible for the puddler to see through his bath of metal to know how his bottom fettling is wearing, neither can the foundry-man see through the metal as it pours in a thin stream over the lip of his ladle, and certainly in this latter case the metal should be transparent if at all.

Since Dr. Ramsay's letter appeared I have made fruitless endeavours to see through a stream of metal, both from a Bessemer converter and from the ladle of a Siemens furnace, while a number of my friends connected with iron-founding have been good enough to try experiments for me also, but hitherto without observing any transparency. In several instances special arrangements have been made to obtain a thin uniform stream of molten metal, behind which objects, such as tools and bricks, have been moved by an assistant. It must of course be remembered that considerable experience is necessary in viewing molten metal if accurate ideas are to be obtained, but hitherto my most experienced friends have not been able to see through a uniform thin stream of metal. Hence though I am not at present prepared to deny the truth of Dr. Ramsay's statement, still it would appear that, if molten cast-iron is transparent at all, this transparency can only be observed under exceptional conditions.—I am, &c.,

THOMAS TURNER.

Mason College, Birmingham,
April 4, 1887.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 11, March 14, 1887.

**Artificial Production of the Ruby.**—M. Fremy.—The author refers to his former memoir (1877) and then describes researches which he has lately undertaken in conjunction with M. Verneuil to determine the action of fluorides upon alumina. At a red heat almost all fluorides occasion the crystallisation of alumina. Calcium fluoride thus affects twelve times its weight of alumina. M. Fremy finds that alumina, even without being in actual contact with calcium fluoride, but merely exposed to the vapours given off by the latter when calcined in the air, becomes mineralised, loses its amorphous condition, and is changed into a crystalline mass.

**Variations of the Absorption Spectra of Didymium.**—H. Becquerel.—(See CHEMICAL NEWS, vol. lv., p. 148).

**Researches on the Application of the Rotatory Power to the Study of Certain Compounds produced in Solutions of Tartaric Acid.**—D. Gernez.—When tartaric acid and sodium molybdate occur in solution in equal equivalents a substance is formed having a rotatory power 37·57 times that of tartaric acid. It is, therefore, intelligible that in solutions which, for the same weight of tartaric acid, contain less sodium molybdate, the rotation is strictly proportionate to the weight of the inactive substance employed until the solution contains ½ equivalent. The addition of sodium molybdate to a solution containing already equal equivalents of the two substances produces effects which are scarcely appreciable.

**A General Method of Forming Manganites, setting out from the Permanganates.**— G. Rousseau.— Under the prolonged action of heat manganese dioxide reacts upon manganate, which disappears entirely after being submitted to a temperature of 240° for seven hours. The resulting mass, after repeated washing with boiling water, presents a composition approaching that of a potassium pentamanganite.

*Bulletin de la Société Chimique de Paris.*
Vol. xlvii., No. 2, January 20, 1887.

**New Processes for Preparing Crystalline Carbonates.**—L. Bourgeois.—The author gives two procedures in the moist way, both founded on the precipitation of a superheated saline solution by ammonium carbonate. In one method he operates at 150° to 180° upon 0·5 grm. of an amorphous precipitated carbonate reacting upon 2 grms. of an ammoniacal salt, generally a hydrochlorate in presence of 20 c.c. of water. After four or five heatings, followed by slow coolings, complete crystallisation was effected. According to the other method he heats the dilute solutions to be precipitated to about 140° along with an equivalent quantity of urea, which, at this temperature, is hydrated and converted into ammonium carbonate.

**New Process for the Volumetric Determination of Zinc Powder.**—F. Weil.—The author prepares a liquid of copper, of which 10 c.c. contain exactly 0·1 grm. of pure copper. To this end dry in a porcelain capsule pure copper nitrate, the ignition of which is completed over a gas-burner in a platinum crucible. The copper oxide thus obtained is let cool in the desiccator and 12·519 grms. are weighed out and dissolved in pure hydrochloric acid with the aid of heat. The liquid is then made up with distilled water to 1 litre. The normal solution thus prepared contains exactly 0·1 grm. of metallic copper in 10 c.c. By means of a pipette 50 c.c. of this liquid are transferred to a porcelain capsule. Ammonia is then added until there is formed a slight turbidity which does not disappear on stirring, though the liquid is still slightly acid. A portion of the zinc powder, weighing 0·4 grm., is let fall to the bottom of the capsule. This small heap is covered with a platinum wire coiled at its lower part into a flat spiral, whilst the stem rises up out of the bath so that the wire serves to stir the liquid. The zinc precipitates copper, equivalent for equivalent. If the operation is performed in a platinum capsule it does not last more than ten minutes. The end of the reaction is ascertained by means of a fresh piece of platinum wire, with which the powder is touched at the bottom of the capsule. If any zinc remains undissolved the wire is instantly covered with a black or red film. If the wire remains a clear white all the zinc is dissolved and the operation is completed. The platinum wire is then withdrawn and washed with the washing-bottle, and there is poured into the capsule, drop by drop, a little acetic acid to render the liquid clear. It is then decanted into a glass graduated to 100 or 200 c.c. The capsule and the deposit of copper are washed with distilled water, adding the washings to the liquid, and making up the volume respectively to 100 or 200 c.c. The whole is stirred and let settle, if needful, for some minutes. Of this liquid 10 c.c. are placed in a small flask of white glass. Two or three volumes of pure hydrochloric acid are added, and it is titrated at a boil until completely decolourised with a solution of stannous chloride, the value of which has been ascertained by means of a dilute solution of copper containing 0·04 grm. copper per 10 c.c. The result shows the excess of copper in the solution. On deducting it from the 0·5 grm. of copper employed we obtained the weight of the copper precipitated by the zinc, and on multiplying this by the coefficient 1·0236 we obtain the quantity of metallic zinc contained in the 0·4 grm. of zinc powder.

**Battery with Carbon-Electrodes without Metals.**—D. Tommasi and Radignet.—This paper requires the accompanying figures.

**Action of Ethylic Aldehyd upon Resorcine.**—H. Causse.—The product obtained is a yellow crystalline body of the composition $C_{14}H_{14}O_4$, which answers to 1 mol. of aldehyd and 2 mols. resorcine less 1 mol. of water.

**On the Nitro-sulphuretted Saccharine of Fahlberg.**—E. Maumené.—The compound produced according to the method patented by Fahlberg is not a definite chemical compound, but a mixture of at least two principles.

**Determination of Total Nitrogen in Organic Matters.**—M. Raulin.—(See Chemical News, vol. lv., p. 147).

**Novel Process for the Determination of Tannin.**—M. Villon.—This memoir will be inserted at length.

**Regeneration of the Residuary Acid from the Manufacture of Gun-Cotton.**—E. Allary.—The author filters the acids over quartz sand and distils.

*Journal für Praktische Chemie.*
New Series, Vol. xxxv., Parts 1 and 2.

**Determination of Fatty Acids in Soaps.**—Prof. Dr. Bauer.—The author selects two watch-glasses, a larger and a smaller, puts in the larger a thin layer of small glass beads, upon which the smaller watch-glass is set as if in a sand-bath. The whole is weighed together and serves for the reception of the fatty acid. The solution and decomposition are effected in the usual manner, *i.e.*, 5 grms. of fresh (not dried) borings of the soap are placed in a small long-necked boiling flask, holding about 150 c.c., and covered first with concentrated glycerin and heated until the soap is uniformly subdivided. About 100 c.c. of alcohol are then added, and the clear liquid is titrated with hydrochloric acid. After the alkali has thus been determined an excess of acid is added, and the fat, which after some time separates out quite clear and accumulates in the neck of the flask, is removed by means of a pipette provided with a fine point and a caoutchouc pipe and put in the upper of the two watch-glasses which have been heated in the air-bath. The fatty acid adhering to the flask is then washed out by pouring in 2 c.c. of petroleum ether or benzine, shaking well, and adding the solution to the matter in the watch-glass until the weight of these glasses remains constant.

**A Convenient Method of Preparing the Bromised Fatty Acids.**—A. Michael.—The author heats the chloride of a monobasic fatty acid with rather more than the calculated quantity of bromine (in order to form the monobromo-derivative) and a rather large quantity of carbon disulphide in a flask provided with a reflux condenser until the escape of hydrobromic acid ceases. To obtain the acid the chloride is introduced into water and fractionated, whilst the corresponding ether is prepared by introduction into absolute alcohol, precipitation by water, and fractionation. The bromine must have been carefully dried.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

**Analysis of Alum Cake.**—We should be glad to be referred to the most accurate method of analysis of "Alum Cake," made from China clay, for alumina and free sulphuric acid most particularly. Can you tell us any really good and reliable work treating on this subject fully, also on the analysis of China clays? For this information we shall feel most obliged.—C. N. and Co.

## MEETINGS FOR THE WEEK.

Monday, 11th.—Medical, 8.30.
Tuesday, 12th.—Royal Medical and Chirurgical, 8.
—— Photographic, 8.
Wednesday, 13th.—Microscopical, 8.
—— Pharmaceutical, 8.
Thursday, 14th.—Telegraph Engineers, 8.


## GEORGE BELL AND SONS' BOOKS.

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ST. PAUL'S SCHOOL.—An Examination for filling up about Four Vacancies on the Foundation will be held on the 21st April, 1887.—For information apply to Mr. S Bewsher, Bursar, St. Paul's School, West Kensington.

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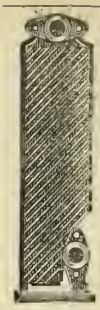

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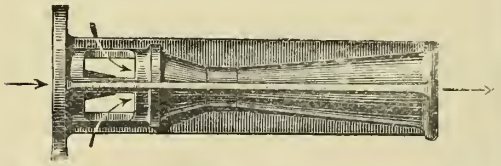

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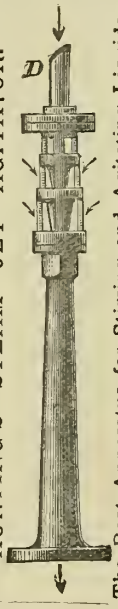


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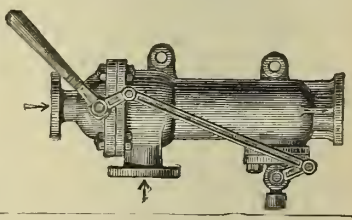

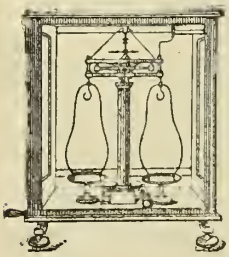

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THE CHEMICAL NEWS.

Vol. LV. No. 1429.

## NOTE ON THE DEVELOPMENT OF VOLTAIC ELECTRICITY BY ATMOSPHERIC OXIDATION.*

By C. R. ALDER WRIGHT, D.Sc., F.R.S.,
Lecturer on Chemistry and Physics,

and C. THOMPSON, F.C.S.,
Demonstrator of Chemistry, in St. Mary's Hospital Medical School.

It is well known that when metallic copper is brought into contact simultaneously with atmospheric air and aqueous solution of ammonia, rapid oxidation is set up, the copper oxide formed dissolving in the liquid, producing a *blue* solution of ammoniacal cupric oxide, or cuprammonium hydroxide. Whilst investigating processes for the manufacture of this fluid (now used commercially on a considerable scale) we noticed that if the air supply be greatly in deficiency relatively to the bulk of the copper, under certain conditions the solution is but little coloured, containing copper dissolved principally as cuprous, and not as cupric, oxide. This might, perhaps, be anticipated *à priori*, inasmuch as it is well known that blue cupric solution in ammonia, when digested with metallic copper in the absence of air, takes up a second equivalent of copper, becoming colourless cuprous solution; but further experiments seem to indicate that the production of cuprous oxide under the oxidising influence of a limited supply of air is the primary action, and not merely a secondary result; in short, that the first step in the change is expressed by the reaction $4Cu + O_2 = 2Cu_2O$; cuprous oxide being formed, which then (under favourable conditions) becomes further oxidised to cupric oxide, thus—

$$2Cu_2O + O_2 = 4CuO,$$

and not by the reaction $2Cu + O_2 = 2CuO$; the cupric oxide thus formed as the first product becoming subsequently reduced (in the absence of air) to cuprous oxide, thus—

$$CuO + Cu = Cu_2O.$$

When a sheet of copper is kept out of direct contact with air by being immersed in ammonia solution, oxidation of the metal is gradually effected by virtue of the dissolving of oxygen from the air at the surface of the fluid, and diffusion of the oxygen solution to the vicinity of the copper. This action is an extremely slow one if the copper be covered by some depth of fluid, and if the setting up of convection currents through heating or evaporation be prevented by keeping the vessel perfectly at rest and at an equable temperature, and well closed to prevent escape of ammonia; but if these precautions be neglected it goes on much more rapidly, and the liquid comparatively soon becomes blue; it can, however, be also materially accelerated by arranging horizontally on the surface of the fluid a plate of platinum or other electrically conducting material not chemically acted upon by the fluid, and connecting this by means of a wire, &c., with the copper plate. The upper conductor, or *aëration plate* as it may be conveniently termed, being simultaneously in contact with the atmosphere and fluid, attracts to its surface a film or aura of condensed gases, the oxygen of which becomes gradually transferred to the copper, a voltaic current circulating through the fluid and connecting wire. Cuprous, and not cupric, oxide thus results, dissolved in the ammonia solution in contact with the copper plate, the mechanism of the reaction being conveniently represented by the scheme—

$$\begin{cases} \text{Copper plate} \quad Cu_2 \mid OH_2 \mid OH_2 \mid O & \text{Aëration plate,} \\ \text{Copper plate} \mid Cu_2O \mid H_2O \mid H_2O \mid & \text{Aëration plate,} \end{cases}$$

water being represented as the electrolyte for simplicity's sake. The air film on the aëration plate being constantly renewed by absorption from the atmosphere, the process goes on continuously as long as the two plates are connected together by the wire. This wire may be lengthened at will so as to make the current which passes through it whilst the action goes on relatively stronger or weaker according to the amount of resistance introduced into the circuit; and by including a galvanometer or silver voltameter in the circuit the ordinary phenomena due to the passage of currents are readily recognisable.

A voltaic cell thus produced "runs down" very rapidly when the resistance in circuit is diminished, more or less recovering when the resistance is again increased; with a large resistance (*e.g.*, sufficient to reduce the current density to a micro-ampère or less per square centimetre of aëration plate surface), a very notable E.M.F. is maintained, amounting under favourable conditions to 0·5 or 0·6 volt. The maximum E.M.F. thus capable of development varies considerably with the strength of the ammoniacal solution, being the less the weaker the fluid; addition of common salt or of sal-ammoniac to the liquid notably increases the E.M.F. and diminishes the internal resistance of the cell. Spongy platinum in a thin layer as the aëration plate gives higher values than thin platinum foil; the highest numbers thus obtained, using pretty concentrated ammoniacal brine, fell but little short of 0·8 volt; or somewhat less than the E.M.F. corresponding with the heat of formation of cupous oxide,* since, according to Julius Thomsen, $Cu_2O$ = 40810 = about 0·88 volt.

It is obvious that this copper atmospheric oxidation cell has a close connexion with the "air-battery" described in 1873 by Gladstone and Tribe (*Roy. Soc. Proc.*, vol. 21, p. 247), in which what is virtually an "aëration plate," consisting of a tray full of crystals of silver, is used, opposed to a copper plate immersed in a solution of copper nitrate. Cuprous oxide is formed in both cases, in virtue of the indirect combination brought about between the oxygen of the air and the copper: but there is this great difference between the two (apart from the cuprous oxide being deposited as such in Gladstone and Tribe's arrangement, and being kept in solution in ours), that in the one the cuprous oxide is formed *at the surface of the copper plate* itself, and in the other *at the surface of the aëration plate*. This essential difference is embodied in the above depicted scheme as compared with the following one which represents the action in Gladstone and Tribe's cell:—

$$\begin{cases} \text{Silver} + O \mid \begin{matrix} Cu(NO_3)_2 \\ Cu(NO_3)_2 \end{matrix} \mid \begin{matrix} Cu(NO_3)_2 \\ Cu(NO_3)_2 \end{matrix} \mid \begin{matrix} Cu \\ Cu \end{matrix} \} \text{ Copper.} \\ \text{Silver} \mid O \begin{Bmatrix} Cu \\ Cu \end{Bmatrix} \mid \begin{matrix} (NO_3)_2Cu \\ (NO_3)_2Cu \end{matrix} \mid \begin{matrix} (NO_3)_2Cu \\ (NO_3)_2Cu \end{matrix} \mid \text{ Copper.} \end{cases}$$

One result of this difference is that the surface of the aëration plate in the ammonia cell is kept constantly the same, whereas in the nitrate cell it is continually changing its character through deposition of solid cuprous oxide on the silver: in consequence of this deposition, whilst the E.M.F. of the ammonia cell, *cæteris paribus*, is constant, that of the nitrate cell is continually varying. Gladstone and Tribe, moreover, only obtained an E.M.F. of $\frac{8}{13}$ to $\frac{11}{13}$ of a Daniell, or about 0·104 to 0·143 volt, even under the most favourable conditions, viz., when the cell was connected with an electrometer; whilst four or five times this amount is indicated by the cells examined by us.

In order to examine separately the fluids collecting round the two plates after action had gone on for some time, we employed cells of U-shape; and to obtain as large an aëration surface as possible we adapted to one

* A Paper read before the Royal Society, March 31, 1887.

* The actual chemical change going on in the cell is the synthesis of cuprosoammonium hydroxide, so that the (unknown) heat of solution of cuprous oxide in ammonia should be added to this to obtain the total heat development.

leg of the U a funnel (as indicated in the figure) with the stem cut off, and united to the U-tube by a piece of india-rubber tubing, *a*, slipped tightly over the junction. The other end of the U tube was closed with an india-rubber cork, *b*, through which passed a piece of glass tubing with a platinum wire, *c*, sealed into it at the lower end and filled with mercury, thus forming a mercury cup, and serving to make contact with the copper plate, *d*, which was soldered to the end of the platinum wire, the soldering and platinum being coated with gutta-percha, so that only the copper plate was in contact with the fluid with which the U-tube was subsequently filled. A similar glass tube and platinum wire mercury cup, *f*, served to make contact with the aëration plate, which was conveniently supported horizontally at the surface of the fluid in the funnel by means of a disk of porous earthenware, *e*; by fixing a rim of gutta-percha round this disk so as to convert it into a sort of tray like the lid of a pill-box, and filling this tray with platinum sponge, an aëration plate of spongy metal was readily obtained. By interposing suitable resistances, galvanometer, silver voltameter, &c., in the external circuit obtained on connecting the two mercury cups by a wire, the current passing could be modified at will, and shown to exhibit all the ordinary phenomena of moderately weak currents.

After continued action with small resistance only in circuit, the liquid in the funnel was found on analysis to contain no copper whatever; whilst that surrounding the copper plate, though colourless before removal from the tube, speedily became blue on exposure to air, and contained more or less considerable amounts of copper in solution, obviously originally in the condition of *cuprous* oxide, $Cu_2O$.

Following up the ideas suggested by the above observations, we are making a number of experiments with a variety of analogous combinations, in which atmospheric oxidation constitutes the essential chemical action taking place; by varying the nature of the aëration plates, the metals dissolved, and the liquids employed (as also by substituting other gases, *e.g.*, chlorine, for air), a large number of combinations are obviously obtainable. Some of those which we have so far examined present points of considerable interest, the oxidising action exerted under favourable conditions being strongly marked: so much so that certain metals, *e.g.*, mercury and silver, not ordinarily prone to atmospheric oxidation, can under suitable conditions be gradually oxidised and dissolved in appropriate liquids, just as the copper is dissolved in the ammonia in the cell above described; these actions, moreover, being accompanied by the development of currents of strength sufficient to cause measurable amounts of electrolytic decomposition outside the cell, *e.g.*, in a silver voltameter.

## NEW PROCESS FOR THE DETERMINATION OF TANNIN.

By M. VILLON.

The determination of tannin presents difficulties: on the one hand, the same process gives different results if applied to extracts of different origin containing the same quantity of tannin, and, on the other, different methods applied to the same extract give different results.

The matter which it is important to determine in practice is the *tannin assimilable in the cold*,—that is, a substance which precipitates albumen and gelatin, which gives coloured precipitates with metallic salts, and which has the property of being absorbed usefully by hides to form leather.

There exist, in extracts along with tannin, allied substances which possess more or less the other properties of tannin, but which want this characteristic—such as gallic, ellagic, glauco-melonic, and gallamic acids, and even a modification of tannin which is produced in presence of gallic acid. Certain methods which do not depend upon the use of hide may determine these substances more or less, and falsify the indications. Even the use of the hide may produce inconvenience, either by giving up to the solution certain principles or by absorbing substances other than the assimilable tannin.

Among the thirty-two known methods for determining tannin that of Hammer, by the difference of the specific gravity of the solution before and after treatment with hide; the method of Müntz, which is merely a modification of the former; and that of Löwenthal, with permanganate, are the only ones which give satisfactory results. The author, instead of hide, uses a solution of lead acetate, suitably diluted, the use of which is more expeditious than that of hide: this process depends on the fact that lead acetate precipitates tannin, and not gallic acid and its allies.

Liebig and Strecker first remarked that a solution of lead acetate gives a yellow precipitate with tannic acid. Stein, in 1857, devised a method for determining tannin by precipitation with a boiling solution of lead acetate in excess. The precipitate was collected and ignited, and the lead oxide weighed, which formed 64 per cent, whence the tannin was readily calculated.

The author finds that the precipitate of lead tannate varies in its composition according to the temperature and the concentration of the solutions. He finds, however, that in a liquid containing a weight of lead acetate equal to three to five times that of the tannin, the precipitate formed has a constant composition. The addition of a small quantity of sodium acetate promotes the formation of the precipitate, which is of a constant composition and is not dissociated by water. Upon these facts he founds the following process:—

Prepare the tannin liquor so that 100 c.c. may contain about 2 grms. of tannin. Prepare a lead liquor by dissolving in heat 100 grms. neutral lead acetate and 20 grms. sodium acetate in 500 grms. water, and making up the solution to exactly 1 litre. Mix in a precipitating glass 100 c.c. of the tannin liquid, 100 c.c. of the lead solution, leave them in contact for five minutes, and filter. Take the sp. gr. D of the lead acetate, the sp. gr. D' of the tannin liquor, and the sp. gr. $\delta$ of the filtered mixture, all at the same temperature. The proportion of tannin in the liquid under examination is then calculated as follows:—If the two liquids mixed without precipitation or alteration in volume the sp. gr. of the mixture would be—

$$\frac{D+D'}{2};$$

but as the lead tannate disappears from the liquid the sp. gr. is diminished, and we find a difference—

$$\frac{D+D'}{2}-\delta.$$

Let $\Sigma$ be the difference of sp. gr. produced in an aqueous solution, of a volume equal to 100 c.c. by the disappearance of the same weight of tannin as that precipitated as lead tannate; probably—

$$\frac{D+D'}{2}-\delta$$

will be proportional to $\Sigma$, whence—

$$\left(\frac{D+D'}{2}-\delta\right)A=\Sigma.$$

This equation permits us to calculate $\Sigma$, if A is determined once for all, and from $\Sigma$ to deduce $p$, the weight of tannin in grammes contained in 100 c.c. of the solution in question, by means of Hammer's table. This table may be summed up in the following formula:—

$$p=\frac{\Sigma}{0{\cdot}00405}.$$

The constant A is not the same for all the tannins: for gallotannic acid it is 50 per cent; for quercitannic acid, 45·3; castaneotannic, 44·8; aspidospertannic, 42·5; abietannic, 40; and catechutannic, 52 per cent.—*Bulletin de la Soc. Chimique de Paris* (vol. xlvii., p. 97).

## ON THE SOLUBILITY OF LITHIUM CARBONATE.

By CARTER NAPIER DRAPER.

Among the few chemists who state it with any approach to precision there is remarkable unanimity as to the solubility of lithium carbonate at ordinary temperatures. Gmelin (citing Vauquelin), Watts, and Fehling concur in giving it as 1 part in 100. Kremer* differs from these authorities, and gives the solubility as 1 in 130 water at 13°. At higher temperatures the solubility is given by—

Kremer, as *less soluble* in hot than in cold water (1 in 128·5 at 100°).
Fehling, as *equally soluble* in hot and cold water.
Vauquelin, as *more soluble* in hot than in cold water.

In presence of these statements, nearly concurrent as regards the cold water solubility and strikingly discrepant as to the solubility in hot water, a re-examination of the facts seemed desirable, and this was undertaken, with the results now to be detailed.

The lithium carbonate employed was prepared in the following way:—The commercial carbonate was dissolved in hydrochloric acid, and the slightly acid solution having—by testing a portion with hydrogen sulphide, and with ammonia and ammonium sulphide—been found to be uncontaminated by the presence of the heavy metals, the remainder was freed from traces of iron, calcium, and magnesium, by successive treatment with ammonia, ammonium carbonate, and lithium hydrate. The solution was then concentrated by evaporation, and the lithium precipitated as carbonate by ammonium carbonate. The precipitate having been washed, first with water and then with alcohol (methylated spirit of sp. gr. 0·830), until the filtrate gave no indication of chlorine, was dried at 100°.† Of this carbonate two distinct solutions were obtained by frequent agitation with distilled water at 15°, during twelve hours. From each of these, two portions of 10 c.c. were measured. On evaporating in platinum, and drying the residue at 100°, the following results were obtained:—

*Solution* I.

*a*. 10 c.c. gave 0·1475 grm. *b*. 10 c.c. gave 0·1475 grm.

*Solution* II.

*a*. 10 c.c. gave 0·1485 grm. *b*. 10 c.c. gave 0·1480 grm.

Giving the solubility of lithium carbonate in water at 15° as 1·4787 per cent.

To determine the solubility at 100°, excess of the carbonate was boiled with distilled water for fifteen minutes, and the solution filtered while hot. About 10 c.c. of the first passing filtrate were rejected, and the quantity to be used having been received in a graduated cylinder provided with a stopper, was allowed to cool, and its volume noted. It was then transferred to a platinum dish, and the cylinder rinsed with distilled water, which was added to the solution. This was then evaporated on a water-bath, and the residue dried at 100° and weighed with the usual precautions. Four experiments gave the following results:—

| | | | | | |
|---|---|---|---|---|---|
| 28 | c.c. gave | 0·1965 | grm. carbonate, or | 0·701 | per cent. |
| 32 | ,, | 0·2350 | ,, | 0·734 | ,, |
| 50 | ,, | 0·3580 | ,, | 0·716 | ,, |
| 42 | ,, | 0·3000 | ,, | 0·714 | ,, |

indicating a mean solubility at 100° of 0·7162 per cent.

The solubility of lithium carbonate at ordinary temperatures is therefore nearly 50 per cent greater than that stated by the authorities above cited; and water at 100° dissolves rather less than one-half the quantity which it is capable of dissolving at 15°.

Dublin, March, 1887.

* *Jahresbericht der Chemie* (quoted by Watts, vol. i., p, 787).

† Operating upon 250 grms. of commercial lithium carbonate, the product obtained was, owing to the solubility of the precipitate in ammonium carbonate, disappointingly small; and even this, to free it from chloride, required no less than *ten litres* of methylated spirit!

## ON THE PHYSICAL PROPERTIES OF MANGANESE STEEL.*

By W. F. BARRETT,

Professor of Experimental Physics in the Royal College of Science for Ireland.

(Concluded from p. 159).

*Breaking Stress.*—Experiments in the breaking stress of the wire were now made. The dynamometer I used was tested and found correct. A comparative experiment was made with pianoforte steel wire, 0·027 inch diameter. This broke at a stress of 150 lbs., corresponding to a breaking stress of 117 tons per square inch. Ordinary steel wire has a breaking stress of 54 to 63 tons per square inch. The tenacity of the best pianoforte steel wire is the highest known, and amounts to 150 tons per square inch.

The *soft manganese steel wire*, No, 19 S.W.G., or 0·96 millimetres in diameter (that is an area of 0·00125 square inch), broke at a stress of 124 lbs., with 18 per cent elongation; the elongation, in fact, was remarkable, being 4 centimetres in 22 centimetres. This breaking stress is equivalent to 48·8 tons per square inch.

The *hard wire* of the same size had a far higher tenacity and far less elongation. The first experiment gave a breaking stress of 280 lbs., or one-eighth of a ton, which corresponds to the enormous *breaking stress of* 110·2 *tons per square inch*. A second experiment gave a breaking stress of 278 lbs., which corresponds to 109·4 tons per square inch, with an elongation of but little over 1 per cent; the ordinary steel wire I tried elongated double this amount. Experiments on the breaking strain of bars of this steel have also been made by Mr. Barnaby, the Admiralty Inspector in Sheffield, who found that the specimen of manganese steel he tried bore a strain of 67 tons per square inch, with the extraordinary amount of 44 per cent elongation before breaking.

High as is this figure, the number I obtained for the wire was far higher, and in fact was so remarkably high that I was anxious for an independent determination with another dynamometer. Mr. H. A. Ivatt, the Locomotive Engineer of the Great Southern and Western Railway Works at Inchicore, kindly undertook this for me, as in their works a new and very accurate dynamometer has recently been erected. Mr. Ivatt found my figure was perfectly correct, and sends me the following statement:—

(See next page).

Mr. Ivatt also tried a specimen of thicker wire, No. 13 gauge; but I had previously spoilt this specimen by testing the effect of heating it to whiteness and quenching in cold water, which rendered the wire soft. This specimen in its soft state, Mr. Ivatt found, had a breaking stress of 47·4 tons per square inch, nearly the same as I found for the fine wire in the soft state. Mr. Ivatt tried to harden it, and writes:—"Heating the No. 13 wire to redness, and allowing it to cool very slowly, is, I find, the only way to harden it." This rendered the wire hard and brittle, and

* A Paper read before the Royal Dublin Society, December 15, 1886.

G. S. & W. R.—Locomotive Department, Inchicore Works, Dublin.

| Expt. | Date. | Description of material, &c. | Standard wire guage. | Area, sq. inches. | Tensile stress. Total lbs. | Tensile stress. Tons per sq. in. | Appearance of fracture. |
|---|---|---|---|---|---|---|---|
| 1. | Dec. 13. | Manganese steel wire, from Prof. Barrett. | No. 19 | 0·00125 | 291 | 103·8 | Hard and brittle. |
| 2. | ,, | ,, ,, | ,, | ,, | 310 | 110·7 | ,, ,, |
| 3. | ,, | ,, ,, | ,, | ,, | 302 | 107·9 | ,, ,, |

Owing to the extremely brittle nature of the metal, the elongation could not be detected.

(Signed), H. A. Ivatt, Locomotive Engineer.

Tested by W. C. Irwin.

apparently lessened its tenacity, for the same wire now broke at a stress of 38·3 tons per square inch.

It will be interesting to compare the tenacity of the manganese steel wire, in grammes per square centimetre, with that of iron and steel. According to Sir W. Thomson (Art. "Elasticity," *Encyc. Brit.*, new edit.), the tenacity or breaking stress of—

| | Grms. per square c.m. |
|---|---|
| Iron wire is .. .. .. .. .. | 625 to 651 × $10^4$ |
| Steel wire .. .. .. .. .. | 859 to 991 × $10^4$ |
| Best pianoforte steel wire .. .. .. | 2362 × $10^4$ |
| Common pianoforte steel wire .. .. . | 1851 × $10^4$ |
| Hard manganese steel wire.. .. .. . | 1735 × $10^4$ |

The two last are my own determinations.

*Electric Resistance.*—I next determined the *electric conductivity* of the wire. For this I employed No. 19 wire, 0·96 m.m. dia., in a length of 510 c.m. This had a resistance of 5·22 ohms, *i.e.*, practically an ohm per metre. The resistance of the hard and soft wire were exactly alike. The specific resistance was 0·000077 of an ohm, or 77,000 C.G.S. units for a cubic centimetre. This is very high: the sp. resistance of ordinary iron is 9827 C.G.S., and of German silver wire 21,170 C.G.S. units per centimetre cube. Experiments are in progress to determine how far its resistance is affected by change of temperature; but, in any case, the remarkably high resistance of manganese steel wire points to a useful application of this material for the construction of resistance coils for electric lighting and other purposes.

I now come to the next and most interesting feature of this steel—its magnetic inertness.

*Magnetic Coefficients.*—Mr. Bottomley, in his note before the British Association to which I have referred, stated that he had submitted the bar of manganese steel to an enormous magnetising force (far beyond what would be necessary to saturate ordinary steel), and after the magnetisation of the manganese steel he had determined its intensity of magnetisation, by the deflection of a mirror magnetometer. The number so obtained showed a magnetic moment $\mu = 2{\cdot}55$ C.G.S. units. Dividing this by the weight of the steel we obtain the magnetisation per gramme, which is 0·013 C.G.S. units. Ordinary steel has a number ranging from 40 to 60, and even up to 100, C.G.S. units per gramme.

Hence the ratio of the intensity of magnetisation in manganese steel to that in ordinary steel is as 1 to 3000, up to 1 to 7700 in the best qualities.

So that the intensity of magnetisation that can be given to manganese steel is, say, 5000 times less than that given to steel of average quality; or if steel be 100,000, manganese steel is 20.

This refers to the degree of permanent magnetism that can be imparted. It is important to know the coefficient, of *induced* magnetism of this remarkable body. This coefficient, designated by K, is the ratio of the intensity of induced magnetisation to the magnetising force of the field, or $K = \frac{i}{H}$: this is now generally termed the *magnetic susceptibility* of the substance.

The experimental determination of this constant, for so feeble a magnetic body as manganese steel, proved a more difficult task than I anticipated, as it is scarcely comparable with iron, and therefore like weighing stones and grains on the same balance.

I first tried the method of torsion adopted by Faraday in the determination of the magnetic force of magne-crystallic bodies, and described by him in the last of his "Experimental Researches in Electricity," *Phil. Trans.*, 1855.

A platinum wire, hung from a graduated torsion head, suspended the specimen under examination in a powerful and uniform magnetic field obtained from a large electro-magnet. A graduated circle was placed below the object under trial, the zero coinciding with the axial position of the object. On exciting the magnet, and then turning the torsion head, the object was twisted out of its axial position, and at last reached a position of unstable equilibrium, when it suddenly swung round to the axial position again, but with reversed ends. The degree of torsion required, *minus* the upsetting angle, was used by Faraday to "measure the force which solicits the body to retain its axial position," that is to say, it is a relative measure of the magnetism induced in the body, or its susceptibility.

A single example out of many experiments will show the working of this method. A piece of manganese steel wire 2·15 millimetres diameter and 44 centimetres long, was suspended (by a platinum wire attached to a torsion head) in a uniform and constant magnetic field. On turning the torsion head, the upsetting angle was found to be 60°, and the torsion required for this was 158°. Hence 158° − 60°, or 98°, is the actual force of torsion employed. With a piece of fine iron wire of precisely the same length and 0·2 millimetre diameter, the upsetting angle was 70°, and the torsion required 320°. Hence 320° − 70°, or 250°, was the force required in this case. The ratio of the forces of the two bodies are therefore as 1 : 2·5. The ratio of the volumes of the two substances will be as the squares of their diameters, or as 1 : 115. Assuming the magnetic moment increases as the volume of the bodies, the ratio of the forces multiplied by the ratio of the volumes will express the ratio at the susceptibilities of the two bodies, which gives

1 : 287.

There are, however, some objections to this method of experiment, as the upsetting angle is not the same, and hence the magnetic distribution at two different angles will not be alike in the two cases.

The following method is free from this objection. The force required to turn each of the two substances through a given very *small* angle, when they are suspended in a magnetic field of constant strength, is found: this value (less the angle of deviation), multiplied by the ratio of the volumes of the two bodies, will give the number sought. A mirror was attached to the cradle supporting the body, and by means of a lamp and scale, a very accurate measure of the angle through which the substance was turned could be obtained. A constant current of 7½ amperes was used to magnetise the electro-magnet, a uniform field being obtained between two large upright pole pieces. The torsion required to turn the manganese steel through 18° was in one experiment 42·5°, and in another 42·3°, or a mean of 42·4°. The torsion required to turn the fine iron wire through the same angle was 94°. This, less the angle of deviation, gives a ratio of 1 : 3. In a more powerful field the numbers

were 66° and 68°, or a mean of 67° for the manganese, and 155·5° and 156·5°, or a mean of 156° for the iron, a ratio of 1 : 2·8. The volumes of the bodies being as 1 : 115, the former experiment gives a ratio of the susceptibilities as 1 : 345 and the latter as 1 : 322. *Hence we may say that the manganese steel has about* 330 *times less magnetic susceptibility than soft iron;* or, if iron be 100,000, manganese steel will be about 300—a very different number, it will be observed, from that obtained by Mr. Bottomley, for the intensity of permanent magnetisation of the two bodies.

A few experiments were now made to determine whether this method showed that the magnetic moment was directly proportional to the volume of the material. Half-a-dozen pieces of fine manganese steel wire were cut, of equal lengths, and the upsetting force and corresponding angle determined in each case. The angle being 60°, the upsetting forces, less this angle, were as follows :—

| | Upsetting Force. | Force per piece. |
|---|---|---|
| With 1 piece .. .. .. | 132 | 132 |
| ,, 2 pieces .. .. .. | 236 | 118 |
| ,, 3 ,, .. .. .. | 400 | 133 |
| ,, 4 ,, .. .. .. | 538 | 134 |
| ,, 5 ,, .. .. .. | 664 | 133 |
| ,, 6 ,, .. .. .. | 793 | 132 |

Dividing the upsetting force by the number of pieces in each case, we obtain the force per piece, as shown in the last column. With the exception of the second experiment—which is evidently erroneous—it will be seen that the forces are directly proportional to the number of pieces, and hence to the volume of the body.

Since I began this investigation, Dr. J. Hopkinson has sent me his paper on the "Magnetisation of Iron," read before the Royal Society of London, in April, 1885. Until I received this paper I was unaware that Dr. Hopkinson had been experimenting on the magnetic properties of manganese steel. The method adopted by Dr. Hopkinson to determine the magnetic susceptibility was wholly different from that which I employed, and consisted in measuring the induced current generated by the sudden removal of a small coil of wire that encircled the iron or steel bar under experiment, and which bar had previously been submitted to a powerful magnetising current. The maximum magnetisation of wrought-iron and of manganese steel (with 12·36 per cent of manganese) deduced from Dr. Hopkinson's figures are as 1441 to 5·6, or 258 to 1.

These numbers are fairly in accordance with those I have obtained, viz. 330 to 1, for steel containing 13·75 per cent of manganese. Considering the wide range of the figures in the table given by Dr. Hopkinson, I should imagine that his ratio is somewhat less reliable than the one I have given.

*Other Magnetic Properties.*—It was interesting to ascertain whether the presence of this percentage of manganese in steel deprived it of other well-known magnetic properties. As might be expected, it showed no elongation under magnetisation. It did not exhibit the magnetic tick or sound heard when iron, steel, nickel, or cobalt is magnetised and demagnetised. A more interesting question was whether it would exhibit the anomalous expansion and after-glow which take place in iron or steel wire when they cool to a certain critical temperature, after being heated to whiteness. I have shown that these phenomena are coincident with that temperature when the magnetic state of these metals, destroyed by a high temperature, is resumed on cooling. Careful experiments with the manganese steel wire, heated to a bright whiteness, established the fact that no trace of this anomalous deportment on cooling occurred with this substance. Here then we have a singular and an important link between the magnetic state of a body and its sudden and momentary expansion and reheating, when at the critical temperature. Like manganese steel, the non-magnetic metals—platinum, copper, German silver, silver and gold wire—do not exhibit this phenomenon.*

I have good hope that the experiments here recorded will become a starting-point for further investigation. When we remember that 13 per cent of a non-magnetic metal, *mechanically mixed* with iron or steel, produces but a slight change in the magnetic state of the latter, and then consider the profound magnetic change brought about by 13 per cent of manganese (itself a feebly magnetic metal) when *alloyed* with steel, we are led into speculation as to the nature of magnetism, and why chemical union should destroy the magnetic state. Manganese steel has about the same magnetic susceptibility as ferric oxide; German silver, in like manner, which is an alloy of brass with the magnetic metal nickel, is itself magnetically inert. Why is this? Do the molecules of manganese insulate the imaginary Amperian currents in the iron, and so prevent the molecular movement which invariably accompanies the act of magnetisation? But if so, how? The electric resistance of manganese steel, as a whole, is scarcely 8 times less than iron, but the magnetic power is upwards of 300 times less.

These experiments have also a practical as well as a theoretic interest. From its high tenacity and negative magnetic properties, manganese steel is eminently adapted for the construction of those parts of machines where the magnetic properties of iron or steel are a serious disadvantage—such, for example, as the bed-plates of dynamos.

Moreover, as everyone knows that the deviation of the compass on iron ships is a grave danger in navigation, more especially from the fluctuating character of the sub-permanent magnetism due to the hard iron and steel, the use of manganese steel for the construction of iron vessels and of ironclads in the navy, and for the anchors and chain cables of all vessels, suggests a simple mode of returning to the magnetic safety of our wooden vessels without sacrificing the advantages of iron.†—*Scientific Proceedings of the Royal Dublin Society.*

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Annual General Meeting, March 30th, 1887.*

Dr. Hugo Müller, F.R.S., President, in the Chair.

The President delivered an address, of which the following is an abstract :—

The number of Fellows of the Society is 1508, of whom 30 are honorary foreign members. One foreign member, Professor A. Butlerow, has died during the year; and the Society has lost 12 Fellows by death :—Robert Alexander; Dr. James Apjohn, F.R.S.; Prof. F. S. Barff; Richard Cowper; M. G. Crossmann; H. Sugden Evans; Rev. W. Flett; George Hirst; Dr. A. P. Price; J. A. Phillips, F.R.S.; E. R. Southby; and H. H. Watson.

20 Fellows have withdrawn :—W. E. Benton; T. F. Best; L. M. Deane; A. F. Dimmock; H. W. Field; W. J. Fuller; A. E. Garrod; Norman Graham; Thos. Harrison; Thos. Jamieson; Herbert Jones; Paul Mathews; P. B. Mills; J. D. McCarthy; Dr. A. P. Page; Dr. Robert Smith; G. Tunbridge; James Steel; A. H. Scott White; Philip Wright; and Wm. Cort Wright.

* Nickel, I find, does not exhibit it, contrary to my expectation; but the magnetic state of nickel is lost at a temperature of 330° to 340° C., which is considerably below red heat. Cobalt wire I have not yet been able to obtain.

† When the foregoing Paper was read, Mr. Fletcher Moore, of Kilbride Manor, called attention to the fact that a manganese iron ore mine existed at Kilbride, Co. Wicklow, and stated that from this ore iron had been smelted of great tenacity and high quality.

28 Fellows have been removed on account of arrears:—F. H. T. Allan; P. S. Brown; Robert Blair; Henry Child; G. Crampton; John Dale; Dr. Arthur Gamgee; A. M. Graham; G. Jarmain; R. H. Jude; F. Jordan; Wm. Marriott; J. E. Mayall; J. D. Mucklow; Dr. C. S. Marsden; John McCarthy; A. A. Nesbit; F. J. O'Farrell; Alfred Payne; A. W. Postans; J. E. H. Richardson; F. I. Scard; J. Steiner; K. Takemura; G. Valentine; Stephen Williams; and James Wilson.

110 new Fellows have been elected during the year.

The number of papers communicated to the Society since the last anniversary meeting is the largest on record, being 118, or 5 in excess of the number read in 1880-81, and 14 in excess of the number read last year. The President expresses the opinion that the Society has every reason to be satisfied with the share which it has contributed to the general progress of chemical science, adding that as we contemplate the ceaseless activity in chemical research now manifested all over the world, and which from year to year is continually on the increase, we are, nevertheless, bound to recognise the fact that vast as the work thus accumulated may appear, there remains still much to be accomplished. The more the field is worked the richer will be the harvest.

The numbers of Abstracts and Papers published in the *Journal* during the past five years are given in the following table:—

| | 1881. | 1882. | 1883. | 1885. | 1886 |
|---|---|---|---|---|---|
| General and Physical Chemistry .. .. .. | 219 | 205 | 237 | 331 | 235 |
| Inorganic Chemistry .. | 188 | 189 | 189 | 191 | 223 |
| Mineralogical Chemistry | 135 | 204 | 192 | 201 | 223 |
| Organic Chemistry . .. | 837 | 739 | 939 | 1047 | 1056 |
| Physiological Chemistry | 112 | 73 | 118 | 142 | 100 |
| Chemistry of Vegetable Physiology and Agriculture .. .. .. .. | 270 | 163 | 324 | 218 | 160 |
| Analytical Chemistry .. | 284 | 195 | 256 | 337 | 289 |
| Technical Chemistry .. | 228 | 212 | 286 | 280 | 66 |
| Total . .. .. .. .. | 2273 | 1980 | 2541 | 2747 | 2352 |
| Papers in Transactions.. | 65. | 63. | 57. | 85. | 85. |

After dwelling on the importance of the determination of physical properties, the President gave a brief review of the more noteworthy chemical investigations of the year; and reference was then made to the work of the City and Guilds of London Institute for the advancement of technical education, with which the President of the Chemical Society is *ex officio* associated. Dr. Müller concluded his address with the following statement:—

The mistaken notion is still too prevalent that technical education has to confine itself to the theoretical considerations of known technical processes, and that a more extended acquisition of scientiffc knowledge is not required, It is obvious that a pupil educated on these lines may find by the time he is able to enter on his practical career that the processes with which he has been made acquainted have in the meanwhile become obsolete, and unless his education has been sufficiently comprehensive to enable him to strike out new lines for himself, he will be ill fitted to compete with those who have been educated on a wider basis.

Essential as it is to impart scientific knowledge to the future manager, it is above all necessary to train him by practical work and research in the laboratory how to investigate a subject which may present itself in his daily occupation, whether it be some unexpected development in a new direction, or whether it be some new difficulty which confronts him in carrying out the processes under his direction. It is self-evident that such knowledge and such practical experience in carrying out investigations is not to be attained by merely attending one or two courses in the lecture room or in the laboratory. Those who mean to effectually qualify themselves for such functions can only accomplish this object by devoting years of patient and intelligent work under the guidance of the professor in properly appointed laboratories.

Prof. Odling proposed that the thanks of the meeting be given to the President for his address, and that he be requested to allow it to be printed. This motion was seconded by Dr. Gladstone, and accepted with acclamation by the Fellows present; the President acknowledged the compliment.

Professor Ramsay moved that thanks for their important services be given to the Editor, Sub-editor, Abstractors, and Librarian; the motion was supported by Mr. Dunstan. Mr. Groves replied.

Dr. A. K. Miller and Dr. Rideal were then appointed scrutators, and a ballot having been taken, the Officers and Council for the ensuing year were declared elected. (See p. 154).

The Treasurer, Dr. Russell, gave an account of the Society's financial condition. The receipts by admission fees and subscriptions had been £2999 2s.; by sale of Journal, £369 19s. 2d.; by dividends on invested capital, £305 0s. 9d. The expenses on account of the Journal had been £2026 16s. 9d; on account of the Abstracts of Proceedings, £163 4s. 11d.; on account of the Library, £323 11s. 10d.; on account of the Catalogue, £249; the total expenses being £3416 14s. 2d.; £500 had been invested in Metropolitan Board of Works 3½ per cent stock, and there was a balance in hand of £1301 10s. 3d.

Mr. David Howard moved that the thanks of the Society be tendered to the Treasurer for his services during the past year; Mr. Friswell seconded the motion. The Treasurer in the course of his reply took occasion to point out that the expenses connected with the issue of the circular relating to the Imperial Institute and the collection of contributions thereto would not be borne by the Society, and that his connexion with the fund was a purely private one.

Mr. J. Spiller proposed a vote of thanks to the Auditors, which was seconded by Dr. H. F. Morley, and acknowledged by Mr. Wyndham Dunstan.

A vote of thanks to the Officers, Council, and Committee, was proposed by Mr. Warington, seconded by Mr. Davies, and acknowledged by Dr. Armstrong.

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## ROYAL INSTITUTION OF GREAT BRITAIN.

*General Monthly Meeting, April 4th, 1887.*

His Grace the Duke of Northumberland, K.G., D.C.L., LL.D., President, in the Chair.

The Managers reported that at their meeting on the 7th of March last the following letter from Dr. Tyndall to the Honorary Secretary was read:—

"Hind Head, Haslemere,
March 6th, 1887.

"My dear Sir Frederick Bramwell,

"The year's holiday so graciously and considerately granted me by the Managers will come to an end next month; and it therefore behoves me to state without further delay, for the information of the Managers, how matters stand with me.

"A brief conversation with my friend Sir Frederick Pollock, and my own reflections thereupon, have convinced me that instead of making a statement myself at the Board Meeting on Monday, it will be more expedient to embody what I have to say in a letter to you.

"For more than one-third of a century it has been my privilege to enjoy the unfailing sympathy and encouragement of the Managers and Members of the Royal Institution. It is now my duty to return to their hands the trust which they first committed to me in the spring of 1853. I have come to this resolution on account of the need I feel of thorough rest, and of freedom from engage-

ments, as to lecturing, the non-fulfilment of which would be detrimental to the Institution, and a cause of sore distress to myself.

"Worries connected with building, and other worries inimical to quietude of brain, have for the last few years troubled me much. These are now, for the most part, things of the past, so that the freedom I seek will, I doubt not, soon restore me to good health.

"I returned from Switzerland in October so refreshed and invigorated that I hoped to be able to cope successfully with all the duties then before me. I had assured myself of the friendly aid of Mr. Crookes, and had even arranged to go to Paris to purchase some instruments necessary for my contemplated work. To the end of the year my health continued strong. Then came a long-continued spell of withering easterly winds, which chilled me, dried me up, and brought on an attack of sleeplessness, intense while it lasted, but which, happily, has in great part disappeared with its cause.

"Of my ultimate and complete recovery I entertain little doubt. Still it would be obviously unfair to the Members, as it would be intolerable to myself, to allow the fortunes of our great Institution to depend in any degree upon such caprices of health. It is therefore my desire to make room for a successor whose years and vigour will place him beyond all changes and chances of this kind.

"Of the feelings called forth by my separation from the Royal Institution I have said nothing. But the Managers will understand that my silence in this respect is due, not to the absence of such feelings, but only to the conviction that on the present occasion the less said about them the better.—Believe me, most faithfully yours,

"John Tyndall."

The Managers further reported that at their adjourned meeting on the 21st of March the following Resolutions were adopted:—

*Resolved*, "That the Managers desire to record by this Resolution the expression of their deep regret that the state of Dr. Tyndall's health should have rendered necessary the resignation of his position of Professor of Natural Philosophy at the Royal Institution, and that it should have compelled the Managers to accept that resignation,—and desire at the same time to record the expression of their hope that the relief thus obtained from the arduous duties of the Professorship will conduce to his speedy and complete recovery.

"The Managers also desire that there should be recorded the expression of their thorough appreciation of the unremitting and most valuable services which during the long period of thirty-four years Dr. Tyndall has rendered to the Royal Institution in carrying out the duties of his office—services which not only have upheld and have advanced the position of the Royal Institution, but have benefited science and the world at large.

"The Managers having ascertained without doubt that Professor Tyndall altogether declines to receive any pension or pecuniary testimonial in recognition of his services to the Royal Institution, and that in parting from his long connection with it he desires only to carry with him the friendly recollection and goodwill of the Members,"—

*Resolved*, "That this generous and disinterested refusal to accept any acknowledgment of a pecuniary nature upon the occasion of his retirement cannot fail to increase the feelings of regard and respect which must be entertained for Professor Tyndall's devotion of so much of his life to the important researches which have been prosecuted by him in the laboratories of the Institution, and for the delivery of those eloquent lectures in its theatre which has done so much to support its scientific renown and to increase its prosperity. The Managers, therefore, under the before-mentioned circumstances of Dr. Tyndall's refusal to accept any pension or pecuniary testimonial, resolved that some marked recognition of a permanent character should be given to the opinion entertained of the great value of Professor Tyndall's labours now about to cease, and the Managers trust that it may prove as agreeable to him as it will be honourable to the Institution, if he would kindly comply with a request which they recommend should be made to him, to sit for his bust (in marble), to be placed in the house of the Institution in perpetual memory of his relations with it, and the cost of which should be defrayed by a vote from the general funds of the Institution; and in order further to perpetuate and honour the name of Professor Tyndall in connection with the Institution, the Managers recommend that one of the courses of Lectures delivered annually in the Institution shall be called the Tyndall Lectures."

*Resolved*, "That the Honorary Secretary, in informing Dr. Tyndall of the acceptance of his resignation, do send to him a copy of the foregoing Resolutions."

The Managers further reported that at their meeting held this day the following letter was read:—

"Hind Head, 3rd April, 1887.

"Dear Sir Frederick Bramwell,

"I have halted in my reply to your letter of March 23rd, through sheer inability to express the feeling which the action of the Managers, at their meeting on the 21st, has called into life.

"And my reply must now be brief; for I hardly dare trust myself to dwell upon the 'Resolutions' which you have conveyed to me. Taken in connexion with the severance of my life from the Royal Institution, and with the flood of memories liberated by the occasion, this plenteous kindness, this bounty of friendship, this reward so much in excess of my merits, well-nigh unmans me.

"And, let me add, the noble fulness of style and expression, which I owe to yourself, and in which the goodwill of the Managers takes corporate form, is in perfect harmony with the spirit which it enshrines.

"Of the Managers existent when I joined the Institution, one only remains upon the present Board. The beneficent work of many of them is for ever ended; but I do not forget the sympathy and support which they extended to me during their lives. And now the long line of kindnesses culminates in words and deeds so considerate and appreciative—so representative of their origin in true gentlemanhood, and warmth of heart, that they have almost succeeded in converting into happiness the sadness of my farewell.

"With heartfelt prayers for the long-continued honour and prosperity of the Institution which I have served so long, and loved so well, believe me, dear Sir Frederick, most faithfully yours,

"John Tyndall."

The Managers further reported that it was resolved "That having regard to the distinguished services rendered to the Royal Institution by Dr. Tyndall, he be recommended to the Members for election as Honorary Professor of Natural Philosophy."

It was then moved, and resolved unanimously, "That Dr. Tyndall be nominated for election at the next General Monthly Meeting, on Monday, May 9th, as Honorary Professor of Natural Philosophy."

Arthur Gamgee, M.D., F.R.S., Edward Bagnall Poulton, M.A., F.G.S., F.Z.S., and Miss Frances Harriet Whitehead were elected Members of the Royal Institution.

Six candidates for membership were proposed for election.

The Right Hon. Lord Rayleigh, M.A., D.C.L., F.R.S., M.R.I., was nominated for election as Professor of Natural Philosophy at the next General Monthly Meeting on May 9th.

The following arrangements for the Lectures after Easter were announced:—

John Hopkinson, M.A., D.Sc., F.R.S., B.S., M.Inst.C.E. M.R.I.—Four Lectures on "Electricity." On Tuesdays, April 19, 26, May 3, 10.

Victor Horsley, F.R.S., B.S., F.R.C.S.—Three Lectures on "The Modern Physiology of the Brain and its Relation to the Mind." On Tuesdays, May 17, 24, 31.

The Rev. J. P. Mahaffy, D.D., Professor of Ancient History in the University of Dublin.—Three Lectures on "The Hellenism of Alexander's Empire." Lecture I. on Tuesday, June 7, Macedonia and Greece; Lecture II. on Thursday, June 9, Egypt; Lecture III. on Saturday, June 11, Syria.

Prof. Dewar, M.A., F.R.S., M.R.I., Fullerian Professor of Chemistry, R.I.—Seven Lectures on "The Chemistry of the Organic World." On Thursdays, April 21, 28, May 5, 12, 19, 26, June 2.

R. von Lendenfeld, Ph.D.—Three Lectures on "Recent Scientific Researches in Australasia." On Saturdays, April 23, 30, May 7.

John W. Hales, M.A.—Four Lectures on "Victorian Literature." On Saturdays, May 14, 21, 28, June 4.

## NOTICES OF BOOKS.

*Record of Experiments at Fort Scott, Kansas, on the Manufacture of Sugar from Sorghum and Sugar-Cane in* 1886. By HARVEY W. WILEY. Washington: Government Printing-Office. 1887.

THE results of the experiments made at Ottawa last year having given encouragement to the friends of the sorghum sugar industry, a new series of experiments was undertaken at Fort Scott, for this purpose the Department of Agriculture entered into an agreement with the Parkinson Sugar Co., under which the Department undertook to supply and erect all the necessary machinery for carrying on the process, the Company, on the other hand, finding the necessary buildings and steam power. Accordingly a diffusion battery of fourteen cells was erected, with calorisators and other apparatus as required; each cell held about 1900 lbs. of sorghum chips moderately packed.

After a full description of all the machinery employed come a number of tables showing the results of the analyses of the mill juices, diffusion juices, carbonatated, sulphured, and other juices, waste waters, waste chips, syrups, &c., obtained during the progress of the experiments.

A few experiments were made to determine whether or not double carbonatations could be practised with sorghum juices. When two- to four-tenths of a gramme of lime per litre were left in the juice of the first carbonatation the filtration took place more readily, and the juice was purer. In double carbonatation some additional lime is added to the hot juice from the filter-presses, and the injection of $CO_2$ is continued until the liquid is neutral. Fans were put up to give this method a trial, but, owing to the juice being so rich in glucose, the method of procedure was not found to be applicable.

The analyses of the samples of cane used show very great variations in their composition, varying as they do from a quality of high sugar-producing value to one worthless for this purpose: the general poor character of the cane was, however, owing to its being too ripe.

To determine the amount of sucrose in the cane by direct estimation, fresh sorghum canes were cut into chips, and digested in boiling water in closed vessels for one hour; the results by two methods gave 8·71 and 7·98 per cent, the amounts calculated from the composition of the juice at 89 per cent being respectively 8·68 and 7·82 per cent,—a very close agreement.

The direct estimation of sugar in the chips was made as follows:—48·9 grms. of chips were placed in a flask and water added up to 305 c.c., the fibre occupying about 5 c.c. After heating and shaking for about an hour the liquor was filtered, 100 c.c. (= 16·3 grms. of chips) were treated with acetate of lead, made up to 110 c.c., and polarised. After adding one-tenth, the reading gives the percentage of sucrose present.

The effect of frost on the manufacture is shown by the following figures:—Before the frost the ratio of glucose to sucrose in the diffusion juices was 39·95 per cent, and after the frost it increased to 68·15 per cent, but when once the process of inversion has commenced it goes on easily and rapidly under the combined influence of time and an elevated temperature.

In reviewing the work done Mr. Wiley concludes that the experiments were an absolute failure as far as demonstrating the commercial practicability of manufacturing sorghum sugar. The causes of this failure were, he thinks, due to:—

1st. Defective machinery for cutting the canes and removing the exhausted chips.

2nd. The over-ripeness of the canes, the time that elapsed after cutting before the chips reached the battery, and the hard frost which set in on October 1st.

3rd. The inversion of the sucrose, owing to the chips being under pressure for too long a time.

4th. The process of carbonatation, as employed, secured a maximum of sugar, but failed to make a marketable molasses.

These difficulties can probably be removed, being as they are to a great extent mechanical; but the chief thing to do is, as Mr. Wiley says, to produce a sorghum plant with a reasonably constant percentage of crystallisable sugar: this must be done by improved seed selection.

When these experiments were completed another series was commenced with sugar-cane. The same trouble with mechanical defects was experienced as before, and the temperature for the diffusion used for sorghum (70° C.) was found to be too low with sugar cane; it was therefore gradually raised to 90° C. before satisfactory results were obtained.

Tables of results of analyses similar to those made of sorghum then follow, the results showing in the most convincing manner that this process of treating sugar-cane gives an increased yield of 30 per cent over that obtained by the best milling and subsequent treatment which has ever been practised in any country.

Carbonatation tends to increase the yield in three ways:—

1st. It diminishes the contents of glucose.

2nd. When carefully done there is hardly any loss of sugar, the wasteful process of "skimming" being entirely done away with.

3rd. The action of the excess of lime and its precipitation by carbonic acid on the substances in the juice increase the ability of the juice to crystallise.

Thus, though we regret the failure of the experiments with sorghum, they have been useful in causing plant to be erected which has proved to be so thoroughly successful in working sugar-cane.

*Certain Points in Agricultural Chemistry, considered in reference to the Selection and Application of Manures for the Sugar-Cane in the Island of Barbadoes.* By J. B. HARRISON. Barbadoes: "Globe" Newspaper Office. 1886.

THE pamphlet now before us was read before the Barbadoes General Agricultural Society on Nov. 9, 1886. The cultivation of the sugar-cane is of great importance in that island. The average yield during the last three periods of seven years each has been a production of 47,700, 48,000, and lastly, since the introduction of the new system of manuring, 55,300 hogsheads per annum. Analyses of some of the Barbadoes soils are given, and attention is directed to the facts that while silica, alumina, iron peroxide, lime, &c., are present in large quantities, in each case nitrogen, potash, and phosphoric anhydride are present in only small proportions; and although the quantities per cent removed from the soil by the canes appear

to be very small, yet, when considered as pounds per acre, they are far from being insignificant; 0·1 per cent means about 300 lbs. per acre. In nine inches depth of soil the analysis shows that there is enough potash for 70, enough phosphoric acid for 200, and enough nitrogen for 37 successive crops of sugar-cane, but even all this is not in such a condition as to be available as plant food.

In selecting manures for the sugar-cane, their application must be considered in two lights. The first is in supplying the deficiency of any constituent which may exist, or in other words to put the soil into a condition to bear a good crop of any kind.

Mr. Harrison then discusses what must be done to keep up permanently the present state of fertility. This, he says, is partially done by the nitrogen contained in the rain and dew, by the absorption of ammonia, and possibly, though we do not think there are good grounds for his assumption, by the direct assimilation of nitrogen from the air by the soil; and after carefully going into the amount of manure absorbed by the plant and the quantity contained in the refuse which is returned to the land, he concludes that in order to maintain the standard of excellence there must be added, during the growth or immediately before the canes are planted, manures capable of supplying in an available form 34 lbs. of nitrogen, 44 lbs. of potash, and 25 lbs. of phosphates per acre. Having considered the first kind of manuring he goes on to discuss the second, that of feeding the plant. The object of this is to supply the plant with the manure or food it requires, and that in the most suitable form. This is a more difficult problem than the first one, and to get a thoroughly satisfactory answer it must be tried not only in one soil and in one climate, but in many; however, very little appears to be known with regard to the real manurial requirements of this plant, and reasoning from analogy has to be resorted to in order to get some ground to go on. This reasoning shows that besides chemical manure, a heavy dressing of pen or sheep manure should be applied before planting the canes, bearing in mind that, as the cane itself contains a sufficient supply of nitrogen for the early stages of its growth, a rapidly acting nitrogenous manure is not required; that ammonia salts are not available as food for young plants; and that, as nitrates would be lost by rain and drainage before the young plants were sufficiently developed to require them, the source of nitrogen should be mainly easily decomposable organic matter, such as blood, containing not more than 4 to 4½ per cent of nitrogen. If these and other recommendations are attended to Mr. Harrison hopes that the sugar-cane will still be able to compete with the beet-root, and thus restore the former prosperity of the island.

# CORRESPONDENCE.

## ON A FUNDAMENTAL LAW OF THERMO-CHEMISTRY.

*To the Editor of the Chemical News.*

Sir,—Allow me to correct one or two errors in my paper in the Chemical News (vol. lv., p. 144), which I unfortunately did not notice before. On looking over my first calculations I find that the anomaly supposed to exist in the case of the nitrates disappears on examination, the value for $NaNO_3$ being erroneously stated as 96·220 instead of 106·220. This brings all the nitrates of the monad metals, except thallium, into agreement with the dyad metals, and thallium would agree if its heat of formation be 48·210 instead of 38·210, as no doubt it really is.

Again, I find that the value 124·661 for the reaction 4Am+3Cl, which I used as a starting-point for calculation, is the mean of the results of Thomsen and Favre. As they differ widely it would be better to take Thomsen's result alone, 119·613. This would increase the values of the thermal equivalents by 1·646 for monad, and twice that for dyad metals, while the values for the non-metals would be altered,—not, however, in a way to materially affect the subsequent results.

The following are some of the more important changes: H = 18·619, Cl = 20·706, Br = 9·751; O in hydrates 17·392, in oxides 3 600; S in MSH about −33·938, in $M_2S$ −47·600, in $M_2SO_4$ 135·384; C in $M_2CO_3$ 101·981, and N in all nitrates 5·751.

Other alterations are easily made. My object in the above-mentioned paper was merely to draw attention to the law, and show how the thermal equivalents might be calculated.—I am, &c.,

C. A. Seyler.

## TRANSPARENCY OF MOLTEN IRON.

*To the Editor of the Chemical News.*

Sir,—Mr. Turner (Chemical News, vol. lv., p. 163) has, I think, misunderstood my recent letter regarding the transparency of molten iron (Chemical News, vol. lv., p. 104). I intended no rash assertion, but merely stated the impression produced on myself and on two others who witnessed a casting, that the iron was transparent. The object of my letter was to invite the opinions of others,—not to make a definite statement. I have heard (I forget from whom) that gold in the molten state is transparent and green, and my sole object in writing you was merely to raise the question, so that those whose opportunities are better than mine might be able to confirm or disprove my impression.

I ought perhaps to mention that the temperature of the seemingly transparent iron was not very high, so that one was not dazzled by emitted light.—I am, &c.,

W. Ramsay.

## DRINKING-WATER AND DISEASE.

*To the Editor of the Chemical News.*

Sir,—In view of Dr. Emmerich's experiments as to the effect of drinking the diluted sewage from healthy persons, there would seem to be but small danger lurking in excremental material known to have come from a non-pathological source.

An interesting case has recently come under my observation, which shows conclusively that even normal sewage may not be taken inwardly with impunity. Appended is the analysis of a cistern water from Albany, N.Y. The cistern is of the "filtering" type, the filtering wall being of some thickness. The property is owned and occupied by wealthy persons, and every care has been (presumably) exercised in keeping the premises in good order.

Suspicion was cast upon the water some months ago, but its use was continued under a belief in the cleanliness of the cistern.

Suddenly, with but a few hours warning, the entire household, one person excepted, was prostrated. The symptoms varied from intense nausea to great, if not dangerous, prostration.

Over a month has passed, and yet the effects of the poisoning are, in a measure, felt by those more severely attacked. The one person who escaped was the lady of the house, who did not drink the water.

Among those attacked were several children. Upon investigation it was found that both cistern lining and private sewer were defective, and that more or less direct communication existed between them. Up to the time of this outbreak none of the household had suffered from diarrhœa or kindred troubles, nor could I obtain any history of recent disease of any kind. The children attacked were on a short visit only.

What I particularly desire to call attention to is, that the sewage, which undoubtedly caused the trouble, was *normal*,—probably not *fresh*, but still *normal*.

The absence of nitrates would go some distance, moreover, towards showing that it was not very old.

To my mind the evidence seems pretty strong that "specific" germs are not essential to a sewage in order to make its presence in drinking-water strongly objectionable. It is greatly to be regretted that previous analyses of the water were not obtainable, as thereby it is possible some information might have been secured as to the relation of the figures of the analysis to the "poisoning-point" of the water.

*Analysis: Parts per Million.*

| | |
|---|---|
| Free ammonia .. .. .. .. | 15,000 l |
| Albumenoid ammonia .. .. | 2,800 |
| Chlorine .. .. .. .. .. | 46,000 |
| Nitrates and nitrites.. .. .. | traces |

I am, &c.,

WILLIAM P. MASON.

Rensselaer Polytechnic Institute,
Troy, N.Y., March 26, 1887.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 12, March 21, 1887.

**Red Fluorescence of Alumina.**—Lecoq de Boisbaudran.—The author now maintains that the fine red fluorescence studied by M. Becquerel is due to the presence of traces of chromium in ordinary alumina, and does not belong to the pure earth.

**Use of Coal-Gas as a Constant Source in Experiments on Radiation.**—Edouard Branby.—This memoir does not admit of useful abridgment.

**On Antimony Tartrate.**—M. Güntz.—The author finds that the method of preparing acid antimony tartrate indicated by Peligot, *i.e.*, precipitating with alcohol a saturated solution of antimony oxide in pure tartaric acid does not give a compound of definite and constant composition. He boils, instead, an excess of pure antimony oxide in a solution of pure tartaric acid until the liquid contains 2 mols. of the oxide to 5 mols. of the acid. The result is constant.

**Detection and Determination of Alumina in Wine and in Grapes.**—L. L'Hote.—The author evaporates 250 c.c. of wine down to a syrup in a platinum capsule and adds pure sulphuric acid. The carbonaceous mass after ignition in a muffle furnace at a low temperature, leaves a white ash. The ash is treated in a flask with 15 c.c. of nitric acid with the aid of heat. To the solution are added 100 c.c. of a solution of ammonium nitro-molybdate (prepared with 50 grms. molybdic acid per litre) and raised to a boil. The phospho-molybdic precipitate is filtered off and washed with water containing one per cent of nitric acid. To the filtrate are added ammonia and ammonium sulphide in excess, which keep the molybdenum in solution and throw down alumina and iron. The mixed precipitate is collected on a filter and heated in a platinum boat, first in air, then in a current of dry hydrogen, to reduce the iron oxide; when cold it is submitted to the action of dry hydrochloric acid at a red heat, when the iron is volatilised. The white residue in the boat, which may contain traces of silica, is moistened with hydrofluoric acid and a drop of sulphuric acid and heated to bright redness. The residue is then weighed. To prove that it is really alumina it is ignited before the blowpipe upon charcoal with a drop of solution of cobalt nitrate. All the wines examined (save one) whether plastered or not, were found to contain ponderable quantities of alumina. The same rule holds good with grapes, carefully plucked and washed with distilled water before analysis.

**New Synthesis in the Fatty Series by Means of Aluminium Chloride.**—Alphonse Combes.—By the reaction of aluminium chloride and acetyl chloride the author obtains acetyl-acetylacetic ether, a compound of this ether with aluminium, and an anhydride of diacetonic butyryl-butyrylbutyric acid.

*Journal für Praktische Chemie.*
New Series, Vol. xxxv., Part 3.

**Some Rare Products of the Alkali Manufacture.**—C. Rammelsberg.—The principal of these are specular iron, aluminium-calcium silicate combined with calcium sulphide, calcium silicate, crystallised lime, glauberite, gay-lussite, and crystalline silico-carbonate.

**Studies in Chemical Dynamics.**—W. Ostwald.—From the totality of the author's determinations there appears a complete proportionality between the coefficients of the speed of chemical reaction and the electric conductivity in the bases, as it has been previously ascertained to be the case in the acids.

**New Chemical Examination of the "Kochbrunnen" (so-called Boiling Well) at Wiesbaden and Comparison of the Results with those obtained by the Author in 1849.**—Dr. R. Fresenius.—The quantity of the main ingredients of the Kochbrunnen, the alkaline chlorides, and indeed the chlorides altogether, is practically unchanged in the last thirty-six years. Almost the same may be said of the alkaline-earthy sulphates. Lime and magnesia as carbonates have decreased slightly but perceptibly. Ferrous and manganous oxides have increased. The quantities obtained in 1849 for lithium, arsenic, and phosphoric acids are not comparable, as the methods for their determination then known were not sufficiently accurate. The total yearly amount of solids dissolved in the water of the Kochbrunnen is 1,656,735 kilos.

**Constitution of Trimethylene-tricarbonic Acid.**—A. Michael.—This memoir does not admit of useful abstraction.

**A Further Light on the Researches of Herr Julius Thomsen.**—F. Weil.—The author contends that, as Herr Thomsen, by the use of his heated universal burner, finds the combustion heat of benzol higher by 11,400 cals. than by its volatilisation in a current of cold air, the only conclusion open is that such high values must depend on a transfer of heat from the burner to the calorimeter.

**Indium and Gallium as Transferrers of the Halogens.**—C. Willgerodt.—The author's experiments prove that indium and gallium rank among the good transferrers of halogens, provided that the commercial specimens of these metals are not contaminated with other transferrers.

*Biedermann's Central Blatt für Agrikultur Chemie.*
Vol. xv., Part 10.

**Influence of Woods on the Heat of the Air and of the Soil.**—Prof. Th. Nördlinger.—During the day the air in a wood is cooler than in the open country, but warmer during the night. Hence a forest climate is less extreme than that of the fields. The average annual heat of the soil in woods is decidedly less than in the open.

**Pre-determination of the Minimum Temperature for the Night.**—Dr. Köppen.—In the six months from March to August the lowest temperature for the night is almost exactly equal to the dew-point at 9.30 p.m.

The Microbia of the Soil.—E. Laurent.—The author undertakes to test the conclusion drawn by Duclaux from his experiments, that plants cannot utilise the more complex nutrient matters unless these are resolved into simpler states by the action of microbia. He finds that the activity of microbia in humous soils has a great effect upon the nutrition of plants. It must be remembered that the plants in the sterilised soil would find a certain quantity of assimilable matter which the microbia had produced before their destruction.

The Evaporation of Water from the Soil and from Plants.—F. and H. Marie Davy.—The amount of water carried away by the drains cannot be calculated from the rainfall.

An Examination of the Manurial Value of the Gilchrist and Thomas Slag.—Wrightson and Munro.—From an English source.

Formation of Glykuronic Acid in Fasting Animals.—H. Thierfelder.—Animals suffering hunger still form carbohydrates for which the only source must be the albumen of the body.

Contribution to a Knowledge of the Starch Group.—F. W. Dafert.—Starch cannot be considered as a chemical individual, but as a more or less fluctuating mixture of a number of chemical compounds, such as starch, cellulose, granulose, dextrine, sugar, proteine bodies, amides, fat, and ash. The disputes concerning the formula of starch are idle.

The Occurrence of Cholesterine in Vegetable Fats.—E. Heckel and Fr. Schlagdenhauffen.—From the *Comptes Rendus*.

Occurrence of Cholesterine in the Carrot.—A. Arnaud.—From the *Comptes Rendus*.

Development of the Sugar Beet.—Aimé Girard.—From the *Comptes Rendus*.

Examination of the Seeds of G. arboreum.—M. Sace.—From the *Comptes Rendus*.

New Method of Determining the Fat in Milk,—Dr. A. Cronander.—The apparatus is founded upon Hoppe-Seyler's and Soxhlet's principle of agitating the milk with ether and potash-lye. The fat dissolves in the ether and floats upon the surface. Cronander determines the fat present in the ether, not aræometrically, like Soxhlet, but by evaporating off the ether and measuring the volume of the fat remaining.

On Two Commercial Substitutes for Milk.—Prof. J. König.—Analyses of "Milsaline" and "Lactina-Bowick," two proprietary articles advertised for the nourishment of calves.

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*Journal de Pharmacie et de Chimie.*
Series v., Vol. xv., No 3, Feb. 1, 1887.

Experimental Researches on the Solubility of the Medicinal Salts of Quinine.—J. Regnauld and E. Villejean.—A pharmaceutical paper. The results obtained by the authors are given in the form of tables.

Etherification of Sulphuric Acid in "Eau de Rabel."—M. Gautherand.—A purely pharmaceutical paper.

Detection of Wheat-Starch in Chocolate.—Dr. Pennetier.—The author pulverises 2 grms. of the sample, washes it upon a filter, firstly with water to remove sugar, then with alcohol to extract the colouring-matter, and lastly with ether to eliminate fatty matter. He then dries the filter and grinds up the mass anew, so as to have a perfectly homogeneous powder. He then weighs out 1 c.grm. of this powder and triturates it in an agate mortar successively with one, two . . . six drops of the following liquid :—Distilled water 1 vol., glycerin 2 vols., the whole mixed with 5 per cent of the officinal mixture of iodine. When this reagent has coloured the starch he makes six microscopic preparations so as to utilise the whole of the material. He uses slips of 22 m.m. across and observes with Nachet's object glass No. 5 (old) or 7 (new) and with the eye-piece No. 1. He then counts up in each preparation the number of granules of wheat starch contained in ten microscopic fields. He finds, however, that this method is inapplicable if the adulteration exceeds 10 per cent.

Studies on Cannabine.—Dr. F. Roux.—The author finds that the active part of Indian hemp is the resin. The alcoholic extract produces exciting properties, whilst the ethereal extract is inert.

Sterilisation of Hypodermic Solutions.—M. Girling.—A medical paper.

Urea, Phosphoric Acid, and Sugar: their Relations in Urine.—H. Bretet.—A paper of no special chemical interest.

On Saccharine Urines.—C. Mehu.—Of no chemical interest.

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*Justus Liebig's Annalen der Chemie,*
Vol. ccxxxvii., Part 3.

Condensations of the Aldehyds with Phenoles and Aromatic Amines.—L. Claissen.—The author studies the reactions of β-naphthol and benzaldehyd, of β-naphthol and acetaldehyd, and of benzaldehyd and β-naphthylamine.

Researches on Gold.—G. Krüss.—From the above researches it appears that three stages of oxidation of gold, the existence of which has not hitherto been doubted, cannot be formed. Gold has only three oxides, the aurous, auro-auric, and auric oxides. By the formation of these three stages of oxidation gold takes the intermediate position between platinum and mercury, which accords with its atomic weight.

On Chinoline.—E. Lellmann and H. Alt.—The authors give a comparative table of their chinolin-anacarbonic acid, and of the chinolin-anacarbonic acid of Schlosser and Skraup.

On Chinoxaline Bases.—O. Hinsberg.—The chinoxaline bases are, for the most part, sparingly soluble, and have very characteristic properties, their salts having a yellow or a red colour.

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*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* 4th Série, Vol. i., November, 1886.

This issue contains no chemical papers.

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## MISCELLANEOUS.

Electric Gas Lighting Apparatus.—Among the many applications of electricity which are now being brought before the public we note the introduction, by Messrs. Woodhouse and Rawson, of an automatic electric gas lighter, by which means any kind of gas-burner can be turned on, lighted, and turned off by the action of an electric current; by pressing a button the current is sent round the coils of an electro-magnet, and causes an armature carrying a circuit-breaker to vibrate; at the end of the armature is a pawl which, acting on a ratchet-wheel, causes it to rotate, and thus opens the gas tap; a spark from a coil lights the gas, and when the ratchet-wheel has rotated two-thirds round the commutator shunts the current into another circuit. By pressing a second button the armature again causes the ratchet-wheel to revolve one-third round and cut off the gas. The commutator automatically cuts off the current at the end of either operation. Another form of lighter, which can be fixed to any burner, automatically lights the gas when the tap is turned on by hand.

Influence of Heat upon the Combination of Sodium Monosulphide with Water of Crystallisation.—C. Götlig.—The composition of the compounds formed on treating alcoholic sodium hydroxide with hydrogen sulphide depends not alone on the strength of the alcohol, but directly or indirectly upon the temperature.—*Journ. für Prakt. Chemie.*

Prof. H. G. Seeley's Geological Field Class.—It is intended to form a class, including beginners and advanced students, this summer, in the same way as last year, for the study of Geology near London, to be conducted on Saturday afternoons, by Prof. H. G. Seeley, F.R.S., King's College. The science of Geology has been reduced in its general principles to simple and easily understood rules, a knowledge of which enables the student to take an intelligent interest in the mineral structure of the earth around him, and students so disposed should take advantage of this class for the purpose of practical study. "Fifty years of ever brightening science" has gradually lifted the veil which hung around this study, and shown the forces of nature which have rough hewn and afterwards carved and sculptured the surface of the earth. The country around London is very accessible and suitable for the study of Geology. Even in railway travelling those who have tried it know how pleasant is the art of reading the volume of history unfolded by a railway journey through a rolling country, where the companies have made clean cuttings through strata, which are its successive chapters. Applications for tickets should be made at once to either of the Hon. Secretaries, Nicol Brown, F.G.S., 7, Princess Road, Brownswood Park, South Hornsey, N., or to W. W. R. May, 16, Bethune Road, Manor Road, Stoke Newington, N.

## MEETINGS FOR THE WEEK.

MONDAY, 18th.—Medical, 8.30.

TUESDAY, 19th.—Institution of Civil Engineers, 8.
—— Pathological, 8.30.
—— Society of Arts, 8. "South Africa," by Major-Gen. Sir Charles Warren.
—— Royal Institution, 3. "Electricity," by Dr. Hopkinson, M.A., F.R.S.

WEDNESDAY, 20th.—Society of Arts, 8. "Electric Locomotion," by A. Reckenzaun.
—— Meteorological, 7.

THURSDAY, 21st.—Chemical, 8.
—— Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "The Chemistry of the Organic World," by Prof. Dewar, F.R.S.

FRIDAY, 22nd.—Royal Institution, 9. "The Work of the Imperial Institute," by Sir Frederick Abel, F.R.S.
—— Quekett Club, 8.

SATURDAY, 23rd.—Royal Institution, 3. "The New Zealand Alps," by R. Von Lendenfeld, Ph.D.
—— Physical, 3. "On Delicate Calorimetrical Thermometers, and on the Expansion of Thermometer Bulbs under Pressure," by Prof. Pickering. "Note on Magnetisation," by R. H. M. Bosanquet. "On a Thermo-dynamical Relation," by Prof. W. Ramsay, Ph.D., and Sydney Young, D.Sc.

ERRATUM.—Vol. liv., p. 231, for "G. A. Gozdorf," read "G. A. Goyder."

TO CHEMICAL MANUFACTURERS AND GAS COMPANIES.

The Vestry of the Parish of Lambeth are ready to receive Tenders for the supply, up to the 31st March, 1888, of the following articles, viz.:—

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THE CHEMICAL NEWS.

Vol. LV. No. 1430.

## AN INSTANCE OF THE POSSIBILITY OF DECEPTION BY THE SULPHUR EXTRACTIBLE BY ALCOHOL FROM VULCANISED RUBBER.

By BERTRAM BLOUNT.

In the course of an examination of a sample of indigo-dyed serge for foreign colouring-matters, I extracted the cloth with strong alcohol in a Soxhlet's apparatus, with the view of removing aniline dyes.

The solution thus obtained was reddish blue when hot, becoming much redder on cooling, and depositing a blue substance; subsequent investigation showed, however, that no aniline dye was present, but that the red body retained in solution by the cold alcohol was indirubin, and that the blue substance, which was almost insoluble in cold alcohol, was indigo itself.

Moreover, several other cloths known to be really dyed with indigo only, all yielded a blue solution with alcohol when similarly treated, although in most cases it became colourless on cooling, owing to the indigo being deposited and no indirubin being present.

That this indigo was obtained from the extremely intimate mixture of particles of fibre and dye which is characteristic of such a fast dye-stuff as indigo-blue, and was not derived from any small quantity of loosely adhering indigo that might chance to be present, was shown by the fact that even when the extraction was continued for several hours daily, for more than a week, the cloth still yielded a blue solution to the alcohol.

At the beginning of the extraction the alcohol was more deeply coloured than at a later stage; but a minimum was soon reached, and an approximately constant quantity of colour was removed at each discharge of the Soxhlet's tube, as far as could be judged by the tint of the solution.

I mention these details because I think that the solubility of indigo in hot alcohol, and the consequent need of thoroughly cooling the solution before the presence of an aniline dye can be detected, are not generally recognised.

The flask containing the alcoholic extract from the original cloth was set aside for a few days, when the presence of a small quantity of beautiful colourless needle-like crystals, mixed with the deposited indigo, was observed.

These were collected, the specifically lighter indigo washed away from them with alcohol, and preserved in a small corked tube, their examination being deferred till a larger quantity should be available.

To procure a further supply some more of the cloth was treated with fresh alcohol, but this time directly in a flask, without the intervention of a Soxhlet's tube, as the object in this case was not to thoroughly exhaust the cloth, but merely to obtain—by having the alcohol at its boiling-point in contact with excess of cloth—as strong a solution as possible, so as to ensure the formation of the crystals on cooling.

Several extractions of the cloth were thus made, the resulting solutions mixed and set aside to crystallise; to my surprise nothing but indigo came down, even after standing for many days. A friend then suggested that the solution might be supersaturated, and that the addition of one of the crystals previously obtained might produce the desired effect. A crystal was accordingly added, but without result.

The possibility of the crystals having come from the apparatus itself then occurred to me. If so, it was obvious that something must have been present in the first-used apparatus which was absent in the second. I then remembered that in the former the Soxhlet's tube was connected to the vertical condenser *by a rubber cork*, while that connecting it to the flask was of ordinary cork, and in the latter no rubber at all was present.

It therefore seemed probable that the crystals were *sulphur* derived from that source, an hypothesis which was strengthened by the appearance of the crystals, which, instead of being colourless and nearly transparent, as at first, were now a dingy yellow and opaque: examination showed that this was actually the case.

It is noteworthy that the rubber cork had been previously boiled for some time in dilute caustic soda, to remove free sulphur, and that only its lower end was exposed to the alcohol vapour.

The ease with which sulphur is extracted from vulcanised rubber by hot alcohol and its misleading appearance, were recently the subject of a paper in the Chemical News, by A. G. Bloxam, and my experience only confirms the necessity for guarding against this source of deception.

23, Queen Anne's Gate, S.W.,
April 16, 1887.

## THE HARDNESS OF METALS.*

By THOMAS TURNER, Assoc. R.S.M., F.C.S.,
Lecturer on Metallurgy, Mason College, Birmingham.

### Part I.

For many of the purposes to which metals are applied, the degree of hardness of the material is of the utmost importance. In some cases, as in the preparation of a knife-edge, a tool, or a cutting instrument, hardness is much to be desired; while in other instances, where tenacity is required, and the material has to be worked by a tool, special hardness is undesirable. Unnecessary hardness generally leads to loss of time, and extra expense in tools, and is often accompanied by weakness and brittleness in the material. Extra softness, on the other hand, is accompanied with destruction of wearing surfaces, blunted edges, and often also with diminished tenacity. A ready method for obtaining trustworthy comparisons of hardness is much to be desired.

The usual definition of hardness is somewhat as follows:—"A body is said to be harder than another when it can be used to scratch the latter, but cannot be scratched by it. (Daniell, "Principles of Physics," 1884, p. 230). The same writer further states that "Hardness is a property that cannot be measured." Though some objection is possible to the latter statement, it is well-known that the usual methods of determining hardness are entirely qualitative, and hitherto no accurate system has been proposed by which different degrees of hardness can be satisfactorily compared. The scale of hardness in common use was originally proposed by Moh, and is reproduced here for purposes of reference:—

| | |
|---|---|
| 1. Talc<br>2. Rock salt | Scratched by finger nail. |
| 3. Calcite<br>4. Fluor<br>5. Apatite<br>6. Orthoclase | Scratched by a knife blade. |
| 7. Quartz<br>8. Topaz<br>9. Corundum<br>10. Diamond | May be roughly distinguished by a file. |

We are indebted to Dumas for one of the earliest attempts to classify metals in order of their hardness

* Read before the Birmingham Philosophical Society, Dec. 9, 1886.

(Brande, "Elements of Chemistry," 1848, 534). In the following list most of the common metals are arranged in order of hardness, depending upon the facility with which they can be scratched by various materials. It may be mentioned that window glass has a hardness of 5·6 on Moh's scale:—

| | |
|---|---|
| Titanium, Manganese | Harder than steel. |
| Chromium, Rhodium | Scratch glass. |
| Nickel, Cobalt, Iron, Antimony, Zinc | Scratched by glass. |
| Platinum, Palladium, Copper, Gold, Silver, Tellurium, Bismuth, Cadmium, Tin | Scratched by calc spar. |
| Lead | Scratched by the nail. |
| Potassium, Sodium | Soft as wax, at 15·5° C. |
| Mercury, Liquid. | |

Dumas's list, however, is obviously only valuable as a general guide to the variations in hardness between different metals. It makes no claim to quantitative measurement, and even the order of the arrangement is, in several instances, different to that adopted by later experimenters.

In the case of such metals as are used in the arts, and which require to be turned or filed, the workman can judge pretty accurately of the relative hardness by the behaviour of the material under his tools. But such experience is of little value for accurate observation, as it has no quantitative value, and will to some extent depend upon the workman's previous experience, and the form or character of the tool. One of the earliest attemps to find a numerical value for the relative hardness of metals was made by the officers of the United States Ordnance Department (Reports of experiments on the strength and other properties of metal for cannon, 1856). In these experiments a punch in the form of a pyramid was used, and was pressed on the metal to be tested with a force of 10,000 lbs. The softest metal used for cannon was bronze, and an indentation rather greater than was produced in this material was taken as a standard of comparison. In each case the volume of the indentation was found, and this served as a measure of the hardness. The standard volume was 3·33 cubic tenths of an inch; one half this volume was described as a hardness of 2; one-tenth the volume as a hardness of 10, and so forth.

The following extracts illustrate the results obtained (Pole—"Iron Construction," p.p. 67, 99, 129):—

| | |
|---|---|
| Bronze | 1·36 |
| No. 1 pig-iron | 2·55 |
| Wrought-iron | 3·32 |
| No. 2 pig-iron | 4·15 |
| No. 3 pig-iron | 6·4 |
| Hardest iron tried | 10·1 |

These results are of great interest, not only as the forerunners of others obtained by later experimenters, with very similar methods, but also as being almost the only quantitative observations of the variations in hardness of cast-iron. Other experimenters have been content to speak of "steel," or "cast-iron," as if these substances possessed a definite hardness, while we know, as a matter of fact, that their hardness under different circumstances varies over, at least, several degrees on Moh's scale. But it will afterwards be shown that the method of indentation by pressure really does not give a correct expression of hardness. The amount of metal displaced by a given force will evidently depend, to a considerable extent, upon the tenacity of the material, and so the results quoted above must depend upon the resultant of at least two properties, and are, therefore, not correct expressions of relative hardness (For proof of this see Part III.). Hardness I understand to be the property whereby a body is enabled to blunt or wear away the edge of a tool used upon it. In this it differs from tenacity, which, though increasing the *force* necessary to be employed in cutting, does not wear away the edge of the tool. At a later stage it will be shown that, with metals in a state of purity, tenacity and hardness accompany each other; but this is not the case in alloys or in the various commercial varieties of iron.

In 1859 Messrs. Calvert and Johnson published a very interesting series of results of experiments on "The Hardness of Metals and Alloys" (*Phil. Mag.*, 4th series, xvii., p. 114). The method employed was in reality only a modification of that previously described, though the authors appear to have been unaware of the American experiments. A graduated bar terminating in a steel point was pressed by means of a weighted lever upon the surface to be tested. The point used was conical, being 7 m.m. long, 5 m.m. wide at the base, and 1·25 m.m. wide at the smaller end. The weights were added so as to cause the point to enter the metal operated upon 3·5 m.m. in half an hour. A number of common metals were tested, and also five pretty complete series of alloys. Some of the more important results are as follows:—

| | |
|---|---|
| Staffordshire grey iron (No. 3) | 1000 |
| Steel | 958 (?) |
| Wrought-iron | 948 |
| Platinum | 375 |
| Copper (pure) | 301 |
| Aluminium | 271 |
| Silver (pure) | 208 |
| Zinc ,, | 183 |
| Gold ,, | 167 |
| Cadmium ,, | 108 |
| Bismuth ,, | 52 |
| Tin ,, | 27 |
| Lead | 16 |

In connection with alloys, it was shown that in the zinc-copper, tin-copper, and lead-tin series, the hardness was greater than that calculated from a mixture of the constituents, this being especially noticeable in the copper-zinc series. In the tin-zinc series, on the contrary, the hardness observed was slightly less than that calculated.

In considering these experiments, the objection previously mentioned in connection with the American results must be urged, that it is doubtful if the weight necessary to drive a punch a given distance into the metal would not depend at least as much upon the tenacity as upon the hardness. With this special form of experiment there is the difficulty of making the punch enter exactly 3·5 m.m. in just half an hour, and also the fact that in a number of cases the specimens operated upon broke under the pressure, sometimes even before the point had entered at all. Of the general accuracy of the observations themselves, however, we have proof in their agreement with similar experiments by Bottone.

Bottone (Chem. News, 1873, xxvii., p. 215) also appears to have overlooked the results of previous workers in this direction. Two methods were employed in his determinations, the first identical with that of Calvert and Johnson, except for an improved method of applying the pressure to the steel cylinder, which was made to indent the metal to be tested. The second method Bottone considered perhaps less exact, and was used in the case of brittle metals. A soft iron disc rotating with an invariable velocity was pressed with a constant force against the

metal to be tested. The time necessary to produce a cut of a definite depth was taken as a measure of the hardness of the material. The results may be expressed as follows:—

| | | | |
|---|---|---|---|
| Manganese | 1456 | Aluminium | 821 |
| Cobalt | 1450 | Cadmium | 760 |
| Nickel | 1410 | Magnesium | 726 |
| Iron | 1375 | Tin | 651 |
| Copper | 1360 | Lead | 570 |
| Palladium | 1200 | Thallium | 565 |
| Platinum | 1107 | Calcium | 405 |
| Zinc | 1077 | Sodium | 400 |
| Silver | 990 | Potassium | 230 |
| Iridium | 984 | Diamond | 3010 |
| Gold | 979 | | |

Bottone concluded that the hardness so obtained was proportional to the specific gravity of the metal divided by its atomic weight, and gave a number of examples to prove this statement. To these experiments we have to urge the objection brought against other determinations by a similar method, namely, that the depth of the indentation produced would depend upon the combined tenacity and hardness of the material.

It will be found on comparison of the results of Calvert and Johnson with those of Bottone, that in those cases where the same metals have been separately examined the order of hardness is very similar. This is illustrated in the following list:—

| *Calvert and Johnson.* | | *Bottone.* | |
|---|---|---|---|
| Iron | 948 | Iron | 1375 |
| Platinum | 375 | Copper | 1360 |
| Copper | 301 | Platinum | 1107 |
| Silver | 208 | Zinc | 1077 |
| Zinc | 183 | Silver | 990 |
| Gold | 167 | Gold | 979 |
| Cadmium | 108 | Cadmium | 760 |
| Tin | 27 | Tin | 651 |
| Lead | 16 | Lead | 570 |

It will be seen, however, that the quantitative values of the hardness given by the two series of experiments is very different. Thus, as examples, we have the following approximate values:—

Calvert and Johnson $\frac{Fe}{Cu} = 3\ \frac{Fe}{Pb} = 58\ \frac{Pt}{Zn} = 2\ \frac{Cd}{Sn} = 4$

Bottone $\frac{Fe}{Cu} = 1\ \frac{Fe}{Pb} = 2\tfrac{1}{2}\ \frac{Pt}{Zn} = 1\ \frac{Cd}{Sn} = 1$

It is obvious from these values that the numbers given to represent the hardness of the different metals are only correct under the circumstances of the experiment. An interesting question arises as to the cause of the marked difference in the numerical values obtained. The explanation is probably to be found in the fact that in Calvert and Johnson's experiments the weight was *gradually* applied during the space of half-an-hour. As a natural consequence, plasticity is an important factor, and the plastic metals—tin, lead, and cadmium—yield very low values. Bottone appears to have applied his weights more rapidly, and naturally obtained higher values.

Reference has been made to the fact that the force required to make a given indentation would depend, at least in part, on the tenacity of the material. It is therefore interesting to compare the hardness results previously quoted with the tenacity of the same metals as given by other observers. In 1809 M. Guyton-Morveau published the results of experiments on the tenacity of the common metals, as measured by the weight in kilos., supported by a wire 2 m.m. in diameter (*Annales de Chemie*, 1st series, lxxi., p. 189). To the nearest whole number his results are as follows (p. 194):—

| | | | |
|---|---|---|---|
| Iron | 250 | Gold | 68 |
| Copper | 137 | Zinc | 50 |
| Platinum | 125 | Tin | 16 |
| Silver | 85 | Lead | 6 |

A much more extensive series of experiments was performed in 1841-44, by M. G. Wertheim (*Ann. Chim. et Phys.*, 3rd series, xii., p. 385; xv., p. 114). In the following table is given the tenacity of the commoner metals, the values being in kilos. per square m.m. In each case the metal was annealed, and used in the form of wire, the weights being added quickly:—

| | | | |
|---|---|---|---|
| Iron | 50·3 | Zinc | 14·4 |
| Copper | 31·6 | Gold | 11·0 |
| Platinum | 26·7 | Cadmium | 4·8 |
| Silver | 16·4 | Tin | 3·6 |
| | | Lead | 2·0 |

It is interesting now to compare the results of the different observers. This is done in the following table:—

*Hardness.*

| Moh's Scale. | Calvert and Johnson. | | Bottone. | |
|---|---|---|---|---|
| 5 | Iron | 948 | Iron | 1375 |
| 5—4 | Platinum | 375 | Copper | 1360 |
| 3—2½ | Copper | 301 | Platinum | 1107 |
| 3—2½ | Silver | 208 | Zinc | 1077 |
| | Zinc | 183 | Silver | 990 |
| 3—2½ | Gold | 167 | Gold | 979 |
| | Cadmium | 108 | Cadmium | 760 |
| 2 | Tin | 27 | Tin | 651 |
| 1½ | Lead | 16 | Lead | 570 |

*Tenacity.*

| | Guyton Morveau. | | Wertheim. | |
|---|---|---|---|---|
| 5 | Iron | 250 | Iron | 50·3 |
| 5—4 | Copper | 137 | Copper | 31·6 |
| 3—2½ | Platinum | 125 | Platinum | 26·7 |
| 3—2½ | Silver | 85 | Silver | 16·4 |
| | Gold | 68 | Zinc | 14·4 |
| 3—2½ | Zinc | 50 | Gold | 11·0 |
| | — | — | Cadmium | 4·8 |
| 2 | Tin | 16 | Tin | 3·6 |
| 1½ | Lead | 6 | Lead | 2·0 |

An examination of this table shows that, according to the experiments referred to, the order of the common metals for hardness and tenacity is practically the same. It has previously been mentioned that Bottone stated the hardness of the common metals varied as the specific gravity divided by the atomic weight. But Wertheim had stated thirty years earlier that the *tenacity* of a metal varied as the specific gravity divided by the atomic weight. It will be seen that what Wertheim first stated to be the case in relation to tenacity, Bottone quite independently afterwards claimed to be true of hardness.

The fraction $\frac{\text{atomic weight}}{\text{specific gravity}}$ we know as the "atomic volume," hence $\frac{\text{specific gravity}}{\text{atomic weight}}$ will vary inversely as the atomic volume, or, in other words, as the number of atoms in a given space. Hence the statements of Wertheim and Bottone, if true, would show that both hardness and tenacity vary directly as the number of atoms in a unit space.

It has been previously stated that the method adopted in the determinations of hardness depended, at least to some extent, upon both tenacity and plasticity, and it is doubtful to what extent the method of experiment affected the close agreement between the order of the metals for tenacity and hardness. But in spite of this defect there can be no doubt that the hardness of the common metals does agree pretty closely with their tenacity, and that these vary in some measure with the atomic volume.

It has been suggested that in attempting to measure hardness and tenacity we are only really trying to measure the same force by two different methods. Such an idea is incorrect. Doubtless both hardness and tenacity depend upon cohesion, and this again upon the number of mole-

cules in a given space; but, nevertheless, hardness and tenacity are distinct physical properties. For instance, in the case of cast-iron, special hardness is not accompanied by high tenacity; on the contrary, the tensile strength of a hard iron may usually be increased by rendering the metal softer. Probably a good example of the difference between tenacity and hardness is furnished in the case of a sandstone. Such a material, owing to the hardness of its particles, rapidly wears away the edge of a tool used in working it, while the tenacity is often very low. We see, therefore, that tenacity depends on the strength of the material, *as a whole*, while hardness varies with the tenacity of the *particles* of the mass.

When the tenacity is uniform throughout, or, in other words, when the material is perfectly homogeneous in structure, tenacity and hardness vary together directly as the number of physical atoms.* Hence in the common metals, which are homogeneous, we find tenacity and hardness follow in the same order, and apparently depend upon the same cause. It may be noted that the metal which is least regular in this respect—namely, zinc—is also the most crystalline. Also that annealing, which diminishes the density of a metal, decreases its tenacity and hardness; while the density, tenacity, and hardness increase together by hammering or cold rolling.

In the case of the vast majority of substances, however, some definite crystalline or other structure is met with, and the material corresponds more or less closely to the example of the sandstone previously mentioned,—consequently tenacity and hardness do not follow according to any such simple rule as that above given. Accepting these statements as correct, it follows that in any trustworthy method of determining hardness the results obtained should closely agree with the tenacity in homogeneous substances, while in non-homogeneous materials it should not follow according to any definite rule.

*Conclusions.*

1. That hardness and tenacity are distinct physical properties.

2. That methods for the quantitative determination of hardness, depending on the production of an indentation of considerable size, have the following disadvantages:—

   *a*. The results are influenced by the tenacity of the metal.

   *b*. Owing to plasticity the results vary according to the time taken to produce the indentation.

   *c*. Brittle substances are apt to be broken by the pressure.

3. That in substances which are homogeneous in structure the hardness and tenacity generally vary according to the number of atoms in a given space.

4. That in substances possessing a definite structure the above rule does not hold good.

(To be continued).

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## SUPPLEMENT TO A CATALOGUE OF CHEMICAL PERIODICALS.†

By H. CARRINGTON BOLTON.

### I. Addenda to Titles.

1. Agenda du chimiste. (Established in 1877.)

5. [b] Sachregister zu den drei Jahrgängen 1823, 1824, und 1825 oder Band VII.-XV. des Jahrbuches der Chemie und Physik. Halle, 1826, 8vo.

13. [c] Justus Liebig's Annalen der Chemie und Pharmacie. *From* Vol. 173 (1874) *the words* "und Pharmacie" *are dropped.*

14. Tables de la cinquième série des Annales de chimie (1874-1883) dressées par Gayon. 1 vol. 8vo. Paris, 1885.

92. [b] Annali di chimica [etc.] 80 vols. (I.-LXXX.), 8vo. Milano, 1845-84.
*United with* Rivista di chimica medica e farmaceutica, *and continued under the title*:

[c] Annali di chimica medico-farmaceutica e di farmacologia. Direttori, P. Albertoni, I. Guareschi; Condirettori, A. Pavesi, G. Colombo. Milano, 1885+.

99. Jahresbericht * * * * der reinen Chemie. 1873-81. 9 vols, roy. 8vo. Tübingen, 1874-83.

149. [A] Répertoire de chimie pure et appliquée [etc.]. 4 vols., 8vo. Paris, 1858-62.

*And simultaneously:*

[C] Bulletin des séances de la Société chimique de Paris, publié par Adolphe Wurtz et Felix Le Blanc. 1858-62. 3 vols., 8vo. Paris, 1861-62.

[C] *united with* [A] in 1863 *and with* [B] in 1864, *forming* [a] *as given in the Catalogue.*

[D] Table analytique des matières contenues dans le Bulletin de la Société chimique 1re et 2e Séries, 1858 à 1874, et dans les Répertoires de chimie pure et de chimie appliquée, suivie de la Table alphabétique des auteurs' dressés par Ed. Willm. 1 vol., 8vo. Paris, 1876.

159. Rivista di chimica, medica e farmaceutica. *United* in 1885 *with* Annali di chimica applicata [etc.]. *See* 92 [b].

180. Zeitschrift für physiologische Chemie. Sach- und Namen-Register zu Bund I.-IV., Strassburg, 1882.

### II. New Titles.

183. Bulletin de l'association des chimistes de sucrerie et de distillerie de France et des colonies. 8vo. Paris, 1883+.

184. Bulletin of the Chemical Society of Washington. 2 Nos., January '84 to '87. Washington, [D. C.], 1886-87.

185. Chemiker (Der) und Drogist. Haupt-Organ für Chemiker, Drogisten, Gewerbtreibende, etc. Herausgegeben von H. Krätzer. 4to. Leipzig, 1885+.

186. Chemisch-technischer Central-Anzeiger, Fach- und Handelsblatt für Chemiker, Techniker Drogisten, Apotheker, Fabrikanten. Central-Insertions-Organ für die gesammten chemischen Industriezweige und deren Hilfsindustrieen. Verantwörtlicher Redacteur, Karl Barthel [*later* Otto Prinz]. Sm. fol. Leipzig, 1883-86+.

187. Deutsche Chemiker-Zeitung. Centralblatt für die chemische Praxis und öffentliche Gesundheitspflege. Unter Mitwirkung bewährter Fachgelehrten herausgegeben und redigirt von Breslauer. 4to. Berlin, 1886+.

188. Journal (The) of Analytical Chemistry. Edited by Edward Hart. Associate editors, P. W. Shimer [and] John Eyerman. With the assistance of the following specialists: F. C. Blake, F. W. Clarke, Isaac Ott, V. C. Vaughan, H. W. Wiley. 8vo. Easton, Pa., 1887.

189. Meddelelser fra Carlsberg laboratoriet. Udgivet ved laboritoriets bestyrelse. 2 vols., 8vo. Christiania, 1885-86+.

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* I use the expression "physical atom" to express the idea that the atom of the physicist and chemist are not identical.

† *Annals N.Y. Academy of Sciences*, vol. iii., p. 159 (1885). Also Chemical News, vols. li. and lii.

190. New York Analyst (The). Devoted to the interests of sanitary science, food, medicine, and the suppression of adulteration. Edited by Henry Lassing. 18 Nos., 4to. New York, 1885.

[This is successor to an American reprint of the Analyst, published in London; hence the above is styled: "New Series."]

*From* No. 19, Oct. 1st, 1885, *continued under the title:*—

[a] American Analyst. A popular semi-monthly review devoted to industrial progress, sanitation and the chemistry of commercial products. H. Lassing, editor and publisher. 4to. New York, 1885+.

191. Skandinaviens kemisk-tekniske Centralblad for Danmark, Sverige, Norge og Finland. Redigeret af G. A. Schmidt. 4 vols., 8vo. Kjøbenhavn, 1882-85+.

192. Supplemento annuale alla enciclopedia di chimica scientifica ed industriale, diretto dal Icilio Guareschi. 3 Nos. Torino, 1884-86+.

193. Tokyo Kagakkai Kaishi. [Editor] J. Sakurai. 6 vols., 8vo. Tokyo. June, 1880-86+. [Tokyo Chemical Society's Journal, Tokyo, Japan.]

194. Vierteljahresschrift über die Fortschritte auf dem Gebiete der Chemie der Nahrungs- und Genussmittel, der Gebrauchsgegenstände, sowie der hierher gohörenden Industriezweige. Unter Mitwirkung von Degener, Hochstetter, P. Lohman, Benno Martiny, Paack, Proskauer, Würzburg, L. Aubry, R. Sendtner, H. Will, von Peters, Weigmann, J. Mayrhofer, E. von Raumer, Röttger, herausgegeben von A. Hilger, R. Kayser, J. König, E. Sell. 8vo. Berlin, 1886+.

195. Zeitschrift für die chemische Industrie, mit besonderer Berücksichtigung der chemisch-technischen Untersuchungsverfahren. Herausgegeben von Ferdinand Fischer. Roy. 8vo. Berlin, 1887+.

196. Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandschaftslehre. Herausgegeben von Wilh. Ostwald. Riga und Leipzig, 1887+.

## LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month ending March 31st, 1887.

By WILLIAM CROOKES, F.R.S.,

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

and C. MEYMOTT TIDY, M.B., F.C.S.,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

*To* The Water Examiner, *Metropolis Water Act*, 1871.

London, April 5th, 1887.

Sir,—We submit herewith the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Altogether, the water supply during the past month has been most satisfactory. In the case of one Company's supply, a few of the samples have to be recorded as "slightly turbid," but this turbidity was entirely local, and due to an interference with the mains in the locality from which the samples were taken. The matters in suspension were, moreover, constituted entirely of mineral matter. The remaining samples, including the whole of those supplied from the Thames, were well filtered, clear, and bright. The proportion of organic matter in the water was appreciably below that of the preceding month's supply.

We are, Sir,
Your obedient Servants,

William Crookes.
William Odling.
C. Meymott Tidy.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, April 7th, 1887.*

Mr. William Crookes, F.R.S., President, in the Chair.

Mr. A. H. F. Ruppel was admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. L. C. Daniell, The Brewery, West Bergholt, near Colchester; Frederick William Freeman, Melbourne House, St. Albans; Herbert James Gover, 28, Broad Street, Hanley, Staffordshire; Edward Day Gravill, 106, Loughboro' Park, Brixton, S.W.; Richard Nelson Jones, L.R.C.P., Swansea Hospital, Swansea; Leonard James Reade, 12, Larches Lane, Wolverhampton; Frank Traphagen, Ph.D., Staunton, Va.

The following Papers were read:—

33. "*Researches on the Constitution of Azo- and Diazo-derivatives.* II. *Diazoamido-compounds* (continued)." By R. Meldola, F.R.S., and F. W. Streatfeild.

The authors describe the results of their experiments on the decomposition of the dinitrodiazoamido-compounds and their ethyl-derivatives by cold chlorhydric acid. By a method described in the paper the products can be isolated and identified without the application of heat at any stage. The results show that the decomposition by cold acid takes place in the same manner as with hot acid, the most noteworthy instance being that of the unsymmetrical compound of m. p. 211° and its ethyl-derivative of m. p. 148°, both of which yield the same *mixed products* as when hot acid is employed. Thus the former compound yields *m*- and *p*-nitrodiazobenzene chlorides and *m*- and *p*-nitraniline, and the latter yields the same diazobenzene chlorides, together with two corresponding ethylnitranilides. The two ethyl-derivatives prepared respectively by the action of diazotised *p*-nitraniline upon ethyl-*m*-nitraniline (m. p. 187°) and of diazotised *m*-nitraniline upon ethyl-*p*-nitraniline (m. p. 174—175°) behave in an analogous manner when decomposed by cold acid, the first giving *p*-nitrodiazobenzene chloride and ethyl-*m*-nitraniline and the second *m*-nitrodiazobenzene chloride and ethyl-*p*-nitraniline. The mode of decomposition of the 187° m. p. ethyl-derivative and the facility with which it breaks up thus negatives the idea which had at first been formed as to this derivative being an amidoazo-compound. A more thorough examination of the substance has shown that it possesses all the characters of a true diazoamido-compound. It gives on complete reduction a mixture of ethyl-*m*-phenylenediamine

and *p*-phenylenediamine. A number of the salts of the dinitrodiazoamido-compounds are described in the paper, the chief result to which their examination has led being that only one atom of displaceable hydrogen is present in these compounds. It is pointed out in conclusion that the existence of *three* isomeric ethyl-derivatives containing *p*- and *m*-nitraniline residues is inexplicable by the generally received formula which admits only of the two modifications:—

(*p*) $NO_2 \cdot C_6H_4 \cdot N_2 \cdot Et \cdot C_6H_4 \cdot NO_2(m)$
and (*m*)$NO_2 \cdot C_6H_4 \cdot N_2 \cdot Et \cdot C_6H_4 \cdot NO_2(p)$.

This fact, combined with the difficulty which has hitherto been experienced in accounting for the identity of mixed diazoamido-compounds, has led Professor Meldola to propose a revision of the commonly accepted formulæ of these compounds.

Discussion.

Mr. Groves asked Professor Meldola whether the mixed diazo-compound yielded practically the para- and meta-nitranilines in the same proportions when it was acted on by cold and by hot hydrochloric acid; also whether different preparations of the compound yield the same results—that is, whether the substance is really homogeneous.

Mr. A. G. Green asked Professor Meldola whether the individuality of the compound $C_6H_4(\overset{(3)}{NO_2}) \cdot \overset{(1)}{N_2}H \cdot C_6H_4(\overset{(4)}{NO_2})$ and its ethyl-derivative of m. p. 147° was determined with certainty. Considering the tendency which certain nitro-compounds (*e.g.*, *m*- and *p*-nitraniline) have of forming tolerably stable molecular compounds with each other with fixed melting point lower than those of either constituent, it seemed possible that this diazoamido-compound (and its ethyl-derivative) might be such a molecular compound of the two isomers $C_6H_4(\overset{(3)}{NO_2}) \cdot \overset{(1)}{N} \cdot NH \cdot C_6H_4(\overset{4)}{NO_2})$ and $C_6H_4(\overset{(3)}{NO_2}) \cdot NH \cdot \overset{(1)}{N_2} \cdot C_6H_4(\overset{(4)}{NO_2})$. This would explain the decomposition by acids into *m*- and *p*-diazonitrobenzene and *m*- and *p*-diazonitrobenzene and *m*- and *p*-nitraniline (or their ethyl-derivatives). The ethyl-derivative of m. p. 147° would then be a compound of the ethyl-derivatives of m. p. 175° and 187°. He suggested that the transference of the $N_2$-group from one amine to the other (especially in strongly acid solution as given in Professor Meldola's previous paper) might be explained by assuming that an inverse change to diazotisation can occur in a solution of a diazo-compound, resulting in the partial reproduction of the amine and nitrous acid, which latter would then diazotise the second amine.

Professor Meldola, in reply to Mr. Groves, stated that there was no doubt that the so-called unsymmetrical compound was a definite chemical substance and not a molecular combination of the dipara- and dimeta-compounds. This point had been fully considered in the paper, and the experiments which had led to this conclusion were described therein. With reference to the question whether the same quantities of decomposition products were obtained from all the dinitrodiazoamido-compounds when decomposed by acid under similar conditions, he stated that quantitative experiments had not yet been made, but that it was proposed to extend the work in this direction. As far as could be estimated, however, by the appearance of the precipitates (nitrobenzeneazonaphthols) and the nitranilines, it seemed that the compounds all gave about the same results. The question raised by Mr. Green as to the possibility of the unsymmetrical compound being a molecular combination of the other two dinitro-compounds, was substantially the same as that put by Mr. Groves, and did not therefore call for any further reply. With reference to Mr. Green's other suggestion, that diazobenzene salts might by a reverse action be transformed into aniline and nitrous acid, Professor Meldola said that so far as he was aware there was at present no evidence in favour of such a view, and that even if this assumption were granted it would not help to explain any of the difficulties connected with the diazo-amido-compounds.

34. "*Conjugated Sulphates and Isomorphous Mixtures of the Copper-magnesium group.*" By P. C. Roy, B.Sc.

Miss Aston and S. U. Pickering having recently called in question the accuracy of Vohl's conclusions, which are supported by Rammelsberg's investigation of 1854, the author has analysed the following salts, prepared according to Vohl's directions:—

(1.) Nickel-Cobalt-Potassium Sulphate.
(2.) Zinc-Manganese-Ammonium Sulphate.
(3.) Copper-Iron-Ammonium Sulphate.
(4.) Copper-Cobalt-Potassium Sulphate.
(5.) Copper-Magnesium-Potassium Sulphate.

From the result it would appear (1) that whenever two sulphates of the copper-magnesium group are dissolved together in equal molecular proportions, with the requisite quantity of an alkaline sulphate, and the solution is left to evaporate spontaneously, salts of the type—

$$x(M''SO_4 + M'_2SO_4 + 6H_2O) + y(M''SO_4 + M'_2SO_4 + 6H_2O)$$

are always formed, $x$ and $y$ being small integers. Thus in (1) $x : y = 2 : 1$, in (2) the ratio is as 9:2, and so on.

The first crop of crystals as a rule does not conform to Vohl's formula; in fact, in no single instance is there the ratio of equality between $x$ and $y$. This is strictly in accordance with the behaviour of isomorphous mixtures, for the first crop is always rich in the least soluble component.

The author's conclusions tally with those of Rammelsberg; it is true that his analyses show that in many instances the component sulphates do not occur in *exact* molecular proportions, but this Rammelsberg justly attributes to the fact that it is often difficult to discriminate between any two successive crops.

Discussion.

Mr. Pickering said that Mr. Roy's experimental results entirely confirmed those obtained by Miss Aston and himself, although the conclusions which he deduced from them were very different. It seemed inconceivable that when solutions of the sulphates were mixed in the molecular proportions of 1:1 the crystals obtained should consist of the salts in different but still definite proportions, whereas if they were not mixed in this simple proportion the crystals were indefinite in composition. Mr. Roy's own experiments disproved such a view, for after the first few crystals had been deposited the solution would no longer contain the sulphates in the original proportion or 1:1, and yet Mr. Roy contended that this solution continued to yield crystals of definite composition. The whole question depended on whether an analysis of salts containing only 1·3 to 12 per cent of the metals was sufficiently accurate to determine whether the salt was definite or not. Mr. Pickering considered that it was not so. By taking $x$ and $y$ in the above formulæ to be small integers (not greater than 10), as Mr. Roy does, a formula could be obtained which would represent any indefinite mixture of the sulphates within the limits of analytical error. In the same way the crystals which Mr. Roy obtained from solutions of the copper and nickel salts mixed in indefinite proportions, and to which he says it would be absurd to assign any formula, would correspond exactly with the formula—

$$11CuSO_4, 2NiSO_4, 13K_2SO_4, 78H_2O,$$

if there were an error of only 0·25 per cent in the determination of the copper or 0·44 in that of the nickel; errors much smaller than some of those observed in duplicate analysis. The analysis of these salts, therefore, is quite incompetent to determine whether they are definite or not; it is only by performing whole series of experiments that conclusions of any value can be drawn, and these series, as Miss Aston and Mr. Pickering have shown, prove clearly that the composition of the crystals varies continuously with variations in the circumstances under which they are produced.

35. "*Suboxide of Silver*, $Ag_4O$." By G. H. Bailey and G. J. Fowler.

The authors have repeated the experiments of Wöhler, and find no evidence of the formation of an argentous citrate when argentic citrate is heated to 100° in a current of hydrogen. The change is a progressive one, the citrate undergoing reduction with the formation of $CO_2$ and $H_2O$. In an experiment in which argentic citrate had been exposed to hydrogen at 100° for 36 hours the residue after extraction with ether contained 85·8 per cent of silver, and by carrying the reduction still further there would in all probability be a complete transformation into metallic silver, water, and carbon dioxide, along with itaconic or the kindred acids. The oxide precipitated from the aqueous extract by means of potash contains metallic silver, and is only obtained in quantities too minute to admit of a determination of the relation of silver to oxygen of sufficiently decisive character.

Faraday's suboxide of silver is also described, and found to be a modified form of ordinary oxide of silver.

Discussion.

Dr. Armstrong pointed out that at the recent Naturforscherversammlung at Berlin, von der Pfordten of Munich had adduced evidence in favour of the conclusion that an argentous oxide may be obtained.

36. "*Action of Trimethylene Bromide on the Sodium Compounds of Ethylic Acetoacetate, Benzoylacetate, Paranitrobenzoylacetate, and Acetone Dicarboxylate.*" By W. H. Perkin (jun.), Ph.D.

The sodium compound of ethylic acetoacetate, when treated with trimethylenebromide, is converted into ethylic methyldehydrohexonecarboxylate—

$$CH_3\text{--}C(=O)\text{--}O\diagdown\diagup$$
$$\|$$
$$COOC_2H_5C\cdot CH_2\cdot CH_2\cdot CH_2$$

a colourless oil boiling at 225°.

This ethereal salt on hydrolysis yields the corresponding acid, $C_7H_{10}O_3$ (m. p. 118°).

When treated with hydrobromic acid in the cold, the ethylic salt is converted into alcohol, carbonic anhydride, and the bromide of acetobutyl alcohol, thus :—

$$C_9H_{14}O_3+H_2O+HBr=CO_2+C_2H_5OH+CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2.CH_2\cdot Br.$$

The free acid, $C_7H_{10}O_3$, on boiling with water, is converted quantitatively into carbonic anhydride, and acetobutyl alcohol, thus :—

$$C_7H_{10}O_3+H_2O=CO_2+CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH.$$

Similar results were also obtained with the sodium compound of ethylic benzoylacetate; the principal product of the reaction being an ethereal salt of the formula—

$$C_6H_5\text{--}C(=O)\text{--}O\diagdown\diagup$$
$$\|$$
$$COOC_2H_5\cdot C\cdot CH_2\cdot CH_2\cdot CH_2$$

(crystalline solid, m. p. 60°).

The corresponding acid,—

$$C_6H_5\text{--}C(=O)\text{--}O\diagdown\diagup$$
$$\|$$
$$COOH\cdot C\cdot CH_2\cdot CH_2\cdot CH_2$$

(m. p. 150°), when treated with hydrobromic acid, yields the bromide of benzoylbutyl alcohol,—

$$C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot Br,$$

and when boiled with water is decomposed into carbonic anhydride and benzoylbutyl alcohol,—

$$C_6H_5\cdot CO\ CH_2\cdot CH_2\cdot CH_2\cdot OH.$$

Similar derivatives were obtained from ethylic paranitrobenzoylacetate.

The disodium compound of ethylic acetonedicarboxylate, when treated with trimethylenebromide, is resolved into ethylic methyldehydrohexonedicarboxylate,—

$$COOC_2H_5\cdot CH_2\text{--}C(=O)\text{--}O\diagdown\diagup$$
$$\|$$
$$COOC_2H_5\cdot C\cdot CH\cdot CH_2\cdot CH_2$$

(colourless oil, b. p. 238—240°, 150 m.m.).

On hydrolysis this substance is first converted into its acid ethylic salt, $C_{10}H_{14}O_5$ (crystalline, m. p = 114°), and then into the dicarboxylic acid, $C_8H_{10}O_5$ (m. p. 160°).

The acid ethylic salt on distillation splits up quantitatively into ethylic methyldehydrohexonecarboxylate and carbonic anhydride. The acid, $C_8H_{10}O_5$, when boiled with water, is decomposed into 2 mols. of carbonic anhydride and acetobutyl alcohol, thus :—

$$C_8H_{10}O_5 + H_2O = 2CO_2+CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH.$$

## NOTICES OF BOOKS.

*Our Daily Water-Supply.* By C. E. Parker-Rhodes, late of H.M. Consular Service. London: E. W. Allen, and the Scientific Publishing Co. (Limited).

This little book, like the subject of which it treats, is of a somewhat multiform character, and discusses not alone scientific topics, but also matters not coming within our province.

In his preface the author enters upon the question of monopolies, and ventures upon the statement that "Monopolies are granted to individuals daily under Letters Patent." Now we contend, on the highest legal authority, that a patent cannot be rightfully termed a monopoly. Coke defines a monopoly as a grant or privilege to some person or corporation, by which the public are henceforward deprived of the right of doing something which was formerly open to them. Now a patent, on the contrary, merely secures to some person the right of doing something which was not open to the public, and which was, in fact, utterly unknown to them. Hence we cannot admit that patent-right has anything whatever to do with "the principle of Free Trade."

In successive sections Mr. Parker-Rhodes argues that filter-beds are, from their position, conducive to ill-health, that all surface-water is unwholesome, and that the water of artesian wells may be injurious by reason of the mineral matter in suspension or solution. Filter-beds are, of course, open to contamination from dust suspended in the atmosphere; but it savours of exaggeration to say that they are "surrounded by factories and working-class dwellings." Still less can we admit that all surface-water is unwholesome. The surface-waters from uninhabited and uncultivated districts, such as supply the water-works of Glasgow, Manchester, Leeds, Halifax, and Sheffield, are strikingly free from "germs of living corruption."

Water obtained through chalk, we are told, "is filtered to complete purity as to *insect* life." Elsewhere we read that "there is an impression that, in the process of cooking, the germs of *insect* life are destroyed by the heat of fire or by boiling water"; and again, "it [*i.e.*, soap] must be a source of constant propagation of *insect* life through the agency of soap-lather." Surely the author must be aware that the microbia to which zymotic diseases are now traced are not insects,—not, indeed, generally speaking, animals of any grade, but low vegetable organisms.

Mr. Parker-Rhodes is, however, perfectly right in his remarks on the part played by parasites, and by almost the entire class of two-winged flies, in transferring disease-germs from the infected to the healthy. Dr. B. W. Richardson may indeed tell his hearers to "drink no impure drink, wear no impure clothing, do no impure act." But so long as gnats, house-flies, &c., exist in the land, the most cleanly person is liable to be inoculated with disease from unknown sources. "Purity," by the way, is one of the

catch-words of the day, and, like the rest of them, has its connotation changed to suit the need of the speaker or writer.

The evils of hard water for domestic and industrial purposes are enforced at some length, and the Clark process is recommended as the remedy. To this method there is no conceivable objection where the hardness of the water is due to calcium carbonate held in solution by excess of carbonic acid. Wherever it has been fairly tried—*e. g.*, at Aylesbury—it has proved splendidly successful.

That "hard water conduces to blood-poisoning," and that "epidemics will continue their ravages so long as the water is used in its condition of hardness," are very hazardous propositions. Populous communities possessing a soft water supply are not found to have any well-marked advantages in their sanitary condition as compared with districts which consume hard waters.

Soft water, it is maintained, will not corrode lead water-pipes; yet in three Yorkshire towns, supplied with excellent soft water, the faculty are at present exercised with cases of lead-poisoning, and the water, as drawn from the taps, has been found not free from lead.

The author is of opinion that "our scriptural text 'Cleanliness is next to godliness' could be fully realised." The origin of this proverbial saying is doubtful, but it is certainly not scriptural, unless our most esteemed concordances are very much at fault.

Mr. Parker-Rhodes's subject is one of the utmost importance, and, in spite of Commissioners and Congresses, is still little cared for and little understood.

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*Mineral Physiology and Physiography.* A Second Series of Chemical and Geological Essays, with a General Introduction. By Thomas Sterry Hunt, M.A., LL.D., F.R.S., &c. Boston: S. E. Cassino. London: Trübner and Co.

We have here a number of essays, all of them well worthy of attention, but not all of them fairly to be included under the heads "chemical and geological." These essays treat of "Nature in Thought and Language," the "Order of the Natural Sciences," the "Chemical and Geological Relations of the Atmosphere," "Celestial Chemistry from the Time of Newton," "Origin of Crystalline Rocks," "Genetic History of Crystalline Rocks," "Decay of Crystalline Rocks," "Natural System in Mineralogy," "History of Pre-Cambrian Rocks," "Geological History of Serpentines," and "Iaconic Question in Geology." Of these the first four will probably be considered the most profoundly interesting, touching, as they do, upon the origin of our elements, upon the nature of the chemical process, and the transition from the mineral to the organic. The writer considers that whilst the mode of generation which produces individuals presents no analogy to the phenomena of the formation of chemical species, yet the phenomena of metagenesis and metamorphosis "are to a certain extent prefigured" in the inorganic world.

As regards chemical combination, he rejects as mechanical Kant's view that "combination is inter-penetration, but accepts that of Hagel, that the chemical process is an identification of the different and a differentiation of the identical."

Returning to the question of the boundary line between the mineral and the organic, he quotes in a note the hylozoic views of Rosmini:—"The ultimate particles of matter are animate, each atom having united with it and forming its atomicity, a sensitive principle. When atoms chemically combine their sensitive principles become one. The unit of natural existence is neither force nor matter, but sentience, and through this all the material and dynamical phenomena of nature may be explained. From the unifications of these sensitive particles or elementary souls, which take place in the combinations of matter, higher and higher manifestations of sentience appear, constituting the various activities displayed in crystals, in plants, and in animals." It appears also that the late W. B. Carpenter, writing in Todd's "Cyclopædia of Anatomy and Physiology," contends that organisation and vital activity arise from the natural operation of forces inherent in elementary matter." According to Stallo "all movement is radically vital, and Allman pronounces life "a property of protoplasm." Graham, the discoverer of colloids, declared that "the colloid may be looked upon as the primary source of the force appearing in the phenomena of vitality."

Our author continues that—"When the chemist shall have succeeded by his synthesis in producing a colloidal albumenoid having the same chemical constitution as protoplasm, there is, as Barker has well said, reason to expect that it will exhibit all the phenomena of life which appear in the protoplasmic matter common to plants and animals."

But according to Reinke, protoplasm, as obtained from the fruits of *Ethalium septicum*, contains about forty proximate constituents, including scarcely 30 per cent of albumenoids. We cannot, without some degree of fear and trembling, imagine the constitution of such a complex, nor can we conceive of its originating except from life.

Dr. Hunt would apply to the study of all phenomena which are simply dynamic or chemic the name of abiophysiology, suggesting the term biophysiology for those which are characteristic of life. We must not forget here an appreciation of the views of Oken, as laid down in his "Physio-Philosophy" (*Naturphilosophie*). To follow the author in this survey would take us too far, but there is great truth and force in his remark that "Oken has been the inspirer and the teacher of the teachers of Science."

In the second essay Dr. Hunt lays down a classification of the sciences. In the first or descriptive group fall general physiography, mineral physiography, and biophysiography. The second group is, in like manner, subdivided into general physiology, mineral physiology (which latter includes physics, chemistry, and theoretical astronomy), and biophysiology.

In the essay on the "Chemical and Geological Relations of the Atmosphere" the author refers us to the opinion which he advanced as far back as 1867, that "the dissociation of elements by intense heat is a principle of universal application," and that "the further dissociation of our elements in stellar or nebulous masses may give us evidence of matter still more elementary than that revealed by the experiments of the laboratory." In 1874 he suggested that the green line in the spectrum of the solar corona may be a "more elementary form of matter" liberated by the intense heat of the solar sphere, and possibly corresponding to the primary matter conjectured by Dumas, having an atomic weight one-fourth that of hydrogen." This substance Prof. C. A. Young considers must be a near approach to the *Urstoff* (="protyle") of certain German speculators. It appears that in 1866 Hinrichs argued in favour of the existence of such a primitive matter, from a consideration of the wave-lengths of the spectra of the elements.

The essay on "Celestial Chemistry from the Time of Newton," originally read before the Philosophical Society of Cambridge in 1881, has been reproduced in the Chemical News. It is interesting as affording convincing proof to what a degree Newton anticipated the views of modern physicists and chemists who do not seem to have been acquainted with his writings. There is certainly much less "new under the sun" than we are apt to suppose.

Dr. Hunt's work may be recommended as rich in suggestive matter.

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*On some Physical Constants of Germanium and Titanium.* By L. F. Nilson and Otto Pettersson.

This pamphlet is a reprint from the new *Zeitschrift für Physikalische Chemie*. It appears that the authors were

requested by Prof. Clemens Winkler to determine the atomic heat of germanium. This *savant* had been led, by certain facts in the chemical behaviour of the new element, to suspect that it must belong to the tetravalent group, an opinion which has been fully confirmed by the researches of the authors. They thought it useful, at the same time, to determine the atomic heat of the nearly-allied element titanium, so as to complete our knowledge of the physical constants of the tetravalent group. The folllowing table gives their most important results :—

| Limits of Temperature. | Specific Heat. | | Atomic Heat. | |
|---|---|---|---|---|
| | Ge. | Ti. | Ge. | Ti. |
| 100°—0 | 0·0737 | 0·1125 | 5·33 | 5·40 |
| 211°—0 | 0·0773 | 0·1288 | 5·59 | 6·18 |
| 301·5°—0 | 0·0768 | 0·1485 | 5·65 | 7·13 |
| 440°—0 | 0·0757 | 0·1620 | 5·47 | 7·77 |

From these values it appears that at low temperatures both the elements possess an atomic heat lower by a unit than the normal figure.

All the series of experiments gave the same number for germanium, whilst titanium, even in the second series, reaches the normal atomic heat, and goes far beyond it at highest temperatures. In this respect germanium deviates from the common rule in a very remarkable manner.

The vapour-density of germanium tetrachloride was found to be in three experiments respectively 7·43, 7·46, and 7·44, the theoretical figure being 7·40. The tetraiodide gave at +440° 20·46, and at +658° 17·19, the theoretical value being 20·0. Germanium monosulphide gave at 1100° 3·54, and at 1500° 3·09, the theoretical density being 3·60.

The critical temperature of the vapour of the tetrachloride was found to be 276·9°. The tension of the vapour given in atmospheres ranges from 0·073 at 10·7° to 38 at 276·9.°

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*Eighth Annual Report of the Winnipeg Board of Trade, together with a Statistical Report of the City's Trade for* 1886. Winnipeg : "The Commercial" Office. 1887.

The history of Winnipeg proper dates from the year 1874. Previous to that year it was known as the village of Fort Garry, and, although the population in 1870 (after the collapse of the first "Riel" rebellion) was only 215 souls, this village had been the leading Hudson's Bay Port in the north-west from the beginning of the century.

From the year 1874 the commercial prosperity of Winnipeg has been steadily increasing, and in five years the population had increased from 3000 to 8000, and the value of assessed property from about 2,000,000 dollars to over 3,500,000 dollars.

In the year 1881, however, what is known as the Winnipeg "boom" set in, and, although it was carried to a crazy excess, it was not altogether a bubble without substance, as the influx of actual settlers was immeasurably greater than that of any preceding year. The year 1882 opened with speculation at its highest pitch, but with the spring came a collapse; still the solid progress which had been made was too great to allow the collapse to be sudden, and the decline was so gradual that the real pressure of contraction was not felt until the following year. Real estate was still at a very high figure, the assessed value of property being fixed at 30,000,000 dols., an increase of nearly tenfold in little over three years. Prices and values then began to fall, until, in the mid-summer of 1884, they had reached a more natural level, and a perfectly healthy, though not very active, state of trade once more existed.

The rebellion in 1885, in the north-west, again interrupted trade to a very considerable extent, but the recovery after its close was very marked. The year 1886, which is principally dealt with in this Report, has been one of moderate prosperity and steady improvement, but not sufficiently so to wipe away the lingering impression that some commercial depression still exists.

The total value of exports shows an increase of nearly 800,000 dollars over the previous year, principally due to the larger quantities of wheat and flour which are brought to the Winnipeg market. Prices, however, in this branch of trade do not improve, but the Manitoba millers are to be complimented in having in one year driven United States mill-products out of the British Columbia markets, where before they held undisputed command.

In closing the Report we note that regret is expressed at the want of progress in manufactures, and it is to be hoped that, now the Board is in a position to give better attention to this branch of trade, it will make improvement in this direction one of its principal studies.

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*On the Action, Therapeutic Value, and Use of the New Karlsbad Spring Salt along with its Relation to the Karlsbad Thermal Water.* ("Ueber Wirkung, therapeutischen Werth und Gebrauch des neuen Karlsbader Quellsalzes nebst dessen Beziehung zum Karlsbader Thermalwasser.") By Dr. W. Jaworski. Vienna: The Author.

This pamphlet has no chemical interest. It may be important to physicians who make a speciality of the use of mineral waters.

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## CORRESPONDENCE.

### ON THE NATURE OF SOLUTION.

*To the Editor of the Chemical News.*

Sir,—Professor Pickering's letter under the above title has just been brought under my notice. I regret exceedingly that I have unintentionally misrepresented Professor Pickering's views on solution. I was led to form the opinion that he had "abandoned the *definite* hydrate theory," by the following passages amongst others in his paper published by you last year (Chemical News, vol. liv., p. 215).

"The hydrate theory can be neither rejected nor accepted."

"Dissolution, I believe, is but one of the many results of apparently indefinite chemical combination."

"The evolution of heat accompanying dissolution will still be attributable, as on the ordinary hydrate theory, to the formation of chemical compounds, but the far greater complexity, and, consequently, instability of these, than of atomic hydrates, if I may so call them—"

Professor Pickering has not noticed my use of the word *definite*, or rather he interprets it in a different way, when he speaks of a *definite* molecular hydrate of the salt *probably never existing undissociated*. Surely this is indefinite enough.

There is one passage in his letter which I cannot pass without a protest. It is this—

"Dr. Nicol asks me at what number of molecules or atoms I draw the line for chemical combination."

I did nothing of the kind, as will be seen on reference to your report, which runs thus :—Professor Pickering "now believed in indefinite hydrate-aggregates of one molecule of salt and many hundred molecules of water. Where was the line to be drawn? He (Dr. Nicol) believed at the number of water molecules present in the solution; Professor Pickering stopped short of this : but where ?"

How this can possibly bear the interpretation put upon it by Professor Pickering I fail to see. It was simply an easy mode of pointing out the apparent indefiniteness of his views and what I considered the close approximation of these to mine.

In answer to the remainder of his letter, I can only say

that when reliable experimental evidence and not hypothesis is brought forward in support of his views on solution, I will at once admit that the whole of the water present in a solution is *not* similarly related to the salt.—I am, &c.,

W. W. J. Nicol.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 13, March 28, 1887.

**The Calorimetric Bomb and the Measurement of the Heats of Combustion.**—MM. Berthelot and Recoura.—This method, first described by MM. Berthelot and Vieille in the *Annales de Chimie et de Physique* (vi., 546; and x., 433), has been applied to gases and to sparingly volatile bodies, and may be easily extended to all volatile compounds.

**Variation of the Solubility of Bodies according to the Quantities of Heat Evolved.**—G. Chancel and F. Parmentier.—A reply to a paper read by M. le Chatelier in the session of March 7, 1887.

**Latent Evaporation-Heats of some very Volatile Substances.**—James Chappuis.—This memoir does not admit of useful abstraction.

**Study of the Alkaline Vanadiates**—A. Ditte.—The author describes seven potassium vanadiates, having the respective compositions $VO_5KO$; $2VO_5KO$; $3VO_52KO$; $3VO_5KO$; $VO_52KO$; $VO_53KO$; and $VO_54KO$.

**Double Strontium and Sodium Phosphate and Arseniate.**—A. Joly.—At the moment when the deposit of the double salt takes place the liquid must contain a sodium monophosphate and strontium chloride. A mixture of these two liquids gives at first no precipitate. But in a few moments, especially if the vessel is strongly rubbed, there is produced a crystalline precipitate of a dimetallic phosphate, and acid is set at liberty.

**Certain Ammoniacal Compounds of Cadmium Chloride.**—G. Andié.—On dissolving slowly and with refrigeration cadmium chloride in ammonia at 20 per cent, and passing through it, with constant refrigeration, a current of gaseous ammonia, there are formed anhydrous crystals of the composition $2CdCl,5NH_3$. Compounds have been obtained on other occasions containing definite proportions of water. Copper chloride yields a compound of a similar type.

**Action of Nitric Acid on the Solubility of the Alkaline Nitrates.**—R. Engel.—Nitric acid precipitates sodium nitrate from its watery solution. Each equivalent of nitric acid up to about the thirtieth precipitates, approximately, an equivalent of sodium nitrate. There appears here the joint result of two opposite actions, the one physical and the other chemical. The physical action exists alone when the quantity of acid added is small. The chemical action comes into play only when the proportion of acid becomes more considerable. It occasions at first merely a perturbation of the former phenomenon, but it soon becomes prodominant.

**On the Metallic Propionates.**—Adolphe Renard.—The author obtains propionic acid from the destructive distillation of resin. He has examined the aluminium, ammonium, barium, calcium, cadmium, chrome, cobalt, copper, iron (ferrous and ferric), lithium, magnesium, manganese (mercurous and mercuric), nickel, lead, potassium, sodium, strontium, and zinc salts.

**Action of Hydrogen upon the Nitrogenous Derivatives of Turpentine.**—C. Tanret.—These bodies, the *dihydro-camphenes* $\alpha$, $\beta$, and $\beta'$, agree in their composition and their reactions, but differ in their physical characters.

**Homologues of Acetylacetone: A New General Method of Preparing the Fatty Acetones.**—Alphonse Combes.—The decomposition by potassa of the diacetones, homologues of acetylacetone, furnishes a new method for producing the fatty acetones.

*Journal de Pharmacie et de Chimie.*
Series v., Vol. xv., No 4, Feb. 15, 1887.

**Notes on the Assay of Opium.**—MM. Adrian and E. Gallois.—The author takes a fairly representative sample, renders it homogeneous by pulverisation, and weighs out 5 grms. for determining the insoluble matter, and 50 grms. for the determination of the morphine. The 5 grms. are rubbed up in 50 grms. alcohol at 70 per cent, with which they are left in contact for about twelve hours. At the end of that time the whole is brought upon a filter, accurately tared, and the residue is extracted with alcohol of the same strength until it is completely exhausted. On weighing the dried residue there is found the weight of the water and the soluble matters. The 50 grms. of opium are put into a wide-mouthed flask with a ground glass stopper and accurately tared. We add, immediately, 200 grms. of alcohol at 70° and place the flask in a stove at 25° to 30°, agitating frequently. We make up the necessary weight when the examination of the 5 grms. is terminated, and after the complete disaggregation of the opium the mixture is left to cool for twelve hours. The weight is then carefully verified and made up if there has been any loss by evaporation. We filter and collect 400 grms. of the solution, representing the soluble part of 40 grms. of opium. The morphine is then precipitated with ammonia, washed with alcohol at 40°, dried, treated with chloroform, and dried anew as in Regnault's process, taking care to let it settle for thirty-six hours before collecting it.

**On Saccharine Urines.**—C. Méhu.—This paper requires the six accompanying figures.

**On Ceresine extracted from Ozokerite.**—M. Saurlandt.—Ozokerite is bleached by treatment with sulphuric acid at 180°. The acid is decomposed and the impurities are carbonised. The ozokerite should be previously dried at 130°.

*Revue Universelle des Mines, de la Metallurgie, &c.,*
Vol. xx., No. 3, November and December, 1886.

This issue contains no chemical matter.

*Moniteur Scientifique, Quesneville.*
Series 4, Vol. i., March, 1887.

**Certain New Substances recently introduced into Industrial Chemistry.**—Ivan Levinstein.—From the *Journal of the Soc. of Chem. Industry*,

**Proportion in which Chloride of Lime loses its Active Chlorine.**—From the *Journal of the Soc. of Chem. Industry.*

**On Phosphorus Peroxide.**—E. T. Thorpe and A. E. Tutton.—From the *Journal of the Chemical Society.*

**The Alizarites of Iron and Chrome.**—L. Liechti and and W. Suide.—From the *Journal Soc. Chem. Industry.*

**Manufacture of Methylene Blue.**—Otto Muhlhauser.—The author describes two processes, that with alkali-waste and that with zinc sulphide, both of which are now in use on the industrial scale.

**Natural State and Origin of Petroleum.**—Dr. Kræmer.—The author discusses the theories of Mendeleeff and Bryasson, and of Hœfer.

Action of Oils upon Metals.—J. J. Redwood.—From the *Journal Soc. Chem. Industry*.

Deposits of Ceriferous Clays.—Dr. J. R. Strohecker. —Already noticed.

German Chemical Patents.—Separation of Sugar from Treacle by Means of Lime and Magnesia.—L. Harperath.

Synthesis of a Kind of Sugar, Formose, analogous to Glucose.—O. Loew.

A New Diamido-dinaphthyl.—Dr. Julius.

Process for the Preservation of Yeast.—H. Boehm. —German Patent, 35,752.

Treatment of Tinner's Waste for the Recovery of the Tin.—T. F. Veasey.—V, No. 1002.

Improvements in the Electro-decomposition of the Chlorides, Bromides, and Iodides of the Heavy and the Alkaline Metals.—S, No. 3377.

Preparation of Aluminium and its Alloys. —L. Graubau.—G, No. 3815.

Process for Obtainlng and Separating the Sulphuretted Hydrocarbons derived from Non-saturated Carbides contained in Paraffins and Petroleum Oils, Sulphonic Acids, and Halogenous Combinations derived from these Sulphuretted Hydrocarbons.—Dr. E. Jacobsen.—J, No. 1299.

Process for Converting Heavy Petroleum Oils or Resins into a Material suitable for Oiling Wool.—J. G. Fayollet.—F, No. 2935.

Purification of Oils by Means of a Filtration combined with the Action of Steam.—G. Materne.—M, No. 4665.

Improvement in the Separation and Purification of the Grease of Wool destined for the Preparation of Lanoline.—No name of inventor.—F. No. 2774.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

The Analysis of Alum Cake.—We have received two letters with reference to the query signed "C. N. and Co." appearing in our issue for the 7th inst. Both writers protest that no information should be given to manufacturers and others which may enable them to dispense with the services of professional chemists. Whilst granting that their arguments are not without force, we must point out that the very object of the CHEMICAL NEWS and of all kindred publications, at home or abroad, is the diffusion of correct information on chemical subjects. If analytical processes are not to be made known to outsiders such a work as "Select Methods," by the Editor of this journal, ought to be suppressed, or to be supplied only to *bona fide* members of the profession.

## MEETINGS FOR THE WEEK.

MONDAY, 25th.—Medical, 8.30.
TUESDAY, 26th.—Institution of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.
—— Society of Arts, 8. "Ornamental Glass," by J. Hungerford Pollen.
—— Royal Institution, 3. "Electricity," by Prof. W. E. Ayrton, F.R.S.
WEDNESDAY, 27th.—Society of Arts, 8. "Appliances for Saving Life from Fire," by Arthur W. C. Shean.
—— Geological, 8.
THURSDAY, 28th.—Royal, 4.30.
—— Telegraph Engineers, 8.
—— Royal Institution, 3. "The Chemistry of the Organic World," by Prof Dewar, F.R.S.
FRIDAY, 29th.—Royal Institution, 9. "The Rolling Contact of Bodies," Prof. H. S. Hele Shaw.
—— Society of Arts, 8. "Village Communities in India," by J. F. Hewitt.
SATURDAY, 30th.—Royal Institution, 3. "The Australian Alps and the Origin of the Australian Fauna," by R. Von Lendenfeld, Ph.D.


## GEORGE BELL AND SONS' BOOKS.

COAL-TAR COLOURS: the CHEMISTRY OF. With special reference to their Application to Dyeing, &c. By Dr. R. BENEDIKT, Professor of Chemistry in the University of Vienna. Translated from the German by E. KNECHT, Ph.D., H.M. of the Chemistry and Dyeing Department in the Technical College, Bradford. 5s.

"This is an excellent little practical manual, dealing with a subject of great scientific and industrial importance. . . . . We cordially recommend the book."—*Nature*.

The ALKALI MAKERS' POCKET-BOOK: Tables and Analytical Methods for Manufactures of Sulphuric Acid, Nitric Acid, Soda, Potash, and Ammonia. By GEORGE LUNGE, Ph.D., Professor of Technical Chemistry, Zurich; and FERDINAND HURTER, Ph.D. Crown 8vo. 7s. 6d.

"It is a work which must of necessity find a place on the shelves o every chemist dealing with the subject."—*Analyst*, Dec., 1884.

EXPERIMENTAL CHEMISTRY. Founded on the Work of Dr. J. A. STÖCKHARDT. A Handbook for the Study of Science by Simple Experiments. New Edition. Revised by C. W. HEATON, F.I.C., F.C.S., Lecturer on Chemistry in the Medical School of Charing Cross Hospital, and Examiner in Chemistry to the Royal College of Physicians. Small post 8vo. 5s.

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The Vestry of the Parish of Lambeth are ready to receive Tenders for the supply, up to the 31st March, 1888, of the following articles, viz.:—

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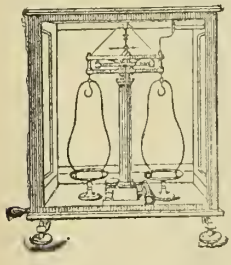

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THE CHEMICAL NEWS.

VOL. LV. No. 1431.

## NOTE ON BISMUTHIC GOLD ("BLACK GOLD")

By R. W. EMERSON MACIVOR, F.I.C., F.C.S., &c.

SOME years ago I had the pleasure of inspecting an excellent little collection of auriferous and other minerals belonging to Mr. C. MacIntyre of Baringhup, and among the specimens to which my attention was particularly called was a small quantity of what the miners called "black gold." This mineral, which my friend Mr. J. Cosmo Newbery, of Melbourne, had found to contain gold and bismuth only, and had named maldonite, was in the early days found associated with the gold obtained from the interesting "Nuggety Reef," Maldon, Victoria, and it was from this quarter that Mr. MacIntyre had obtained it. I learned that it was chiefly found in the granite veins that occur in the quartz composing the reef.

Having been presented with a few grains (0·285 grm.) of the ore, I examined it as thoroughly as was possible. It was without crystalline character that I could detect. It was malleable, and when newly broken had a bright silvery-white lustre, but on lengthened exposure to the air it slowly tarnished, becoming ultimately nearly black. Heated on charcoal it readily melted, and, after roasting in the oxidising flame, left a bead of gold, the charcoal being coated with the familiar film of oxide of bismuth. Sulphur and tellurium were absent. When dissolved in nitro-hydrochloric acid, the ore was found to contain a little siliceous matter. Analysis gave the following results:—

| | |
|---|---|
| Gold .. .. .. .. | 64·211 |
| Bismuth .. .. .. | 34·398 |
| Siliceous matter.. .. | 1·391 |
| | 100·000 |

If the silica be omitted and the metals calculated to make up 100, these results would indicate that the mineral has the formula $Au_2Bi$:—

| | Found. | Theory. |
|---|---|---|
| Gold .. .. | 65·117 | 65·322 |
| Bismuth .. | 34·883 | 34·678 |
| | 100·000 | 100·000 |

I hope to have an early opportunity of further examining this interesting natural alloy.

## THE ASH OF *BOVISTA GIGANTÆA*.

By F. NETTLEFOLD, F.C.S.

THE reputation of this fungus in "Rural Pharmacy," when dried as a styptic, led to an investigation of the ash.

These are dome-shaped, stalkless fungi, growing close to the ground in masses of the more luxuriant grass, which it is possible the mineral matter they collect from the soil may help to flourish.

Their size is about 12"—16" diameter. They are invested in a tough membranous integument, containing chiefly cellular tissue.

| | |
|---|---|
| Dry substance at 100.. .. | 8·35 per cent. |
| Water .. .. .. .. .. | 91·65 |
| Ash .. .. .. .. .. | 0·571 |
| „ on the dry substance .. | 6·36 |

*Analysis of the Ash.*

| | Calculated on plant. | Calculated on residue. |
|---|---|---|
| Insoluble residue in HCl .. | 0·00 | |
| Alumina .. .. .. .. | 0·107 | 15·66 per cent. |
| Magnesia .. .. .. .. | 0·020 | 2·93 |
| $H_2SO_4$ .. .. .. .. .. | 0·060 | 8·79 |
| $SiO_2$ .. .. .. .. .. | 0·003 | 0·44 |
| CaO, mere traces | — | — |
| Phosphate of soda .. .. | 0·381 | 72·18 |

It is noticeable that phosphate of soda is used to stop hemorrhage; and it may be owing to this substance that its reputation is due.

The solution is of an orange colour, and exhales the odour of urea, when heated.

## THE DETECTION AND DETERMINATION OF VANADIUM IN ROCKS AND ORES.

By M. L. L'HOTE.

IN a former memoir (*Comptes Rendus*, Dec. 7th, 1885) the author has given a process for extracting from vanadite the totality of its vanadium in the state of vanadyle chloride, by utilising the different volatility of the chlorides at a given temperature. This process may be applied to the determination of vanadium in rocks and ores.

The method comprises two operations: the extraction of the vanadium as a vanadic solution, and its volumetric or gravimetric determination.

To isolate the vanadium, dry chlorine is passed over an intimate mixture of 4 parts of the sample and 1 part of charcoal, contained in a tube heated to 250° in a special furnace. In case of ores which are almost always arseniferous, the mixture must be previously made into a paste with oil, and calcined at a red heat. When operating upon rocks this precaution is needless. Schlœsing's apparatus is used for generating chlorine.

The tube containing the mixture is connected to a system of condensers, formed of two Mohr's bulb-tubes. As vanadyle chloride in presence of water forms vanadic acid, the presence of vanadium is indicated by the formation of a red coating in that part of the first tube connected directly with the apparatus.

If there is only a very little vanadium in the rock examined, the liquid of the first bulb is not coloured. The vanadium may be detected by dissolving the condensed product in weak hydrochloric acid. The solution on evaporation gives a residue which, if moistened with a drop of colourless ammonium sulphide, takes the purple colour characteristic of vanadium sulphide.

The vanadium is determined by following Margueritte's method applied to the determination of small quantities of iron. We first prepare a standard solution of vanadic acid by dissolving pure vanadic acid in sulphuric acid; 10 c.c. of this liquid represent 0·0028 grm. of vanadium. Numerous experiments have proved that vanadium may be determined, like iron, by reducing the vanadic salt with zinc. The solution of permanganate used is $\frac{1}{1000}$. With such a dilution it is necessary to use certain precautions in order to seize the end of the reaction. The liquids must be hot, and distilled water must be used having no action upon permanganate. Common distilled water always decolourises dilute solutions of permanganate. It is obtained sufficiently pure by re-distilling it over permanganate crystals and preserving it from atmospheric dust.

When the quantity of vanadic acid is high, as in certain ores, the liquid in the first bulb turns a greenish blue. The acid solution, mixed with ammonia and evaporated to dryness, gives a residue which, if heated to redness, may be weighed as vanadic acid.—*Comptes Rendus* (civ., p. 990).

## METHOD OF PREPARING ANHYDROUS METALLIC CHLORIDES.

By H. N. WARREN, Research Analyst.

The following method of preparing metallic chlorides differs from the old method of subjecting the oxide of the metal admixed with charcoal to a high temperature in covered crucibles, and avoids the difficulty of obtaining thereby an intimate mixture of the same:—

Petroleum oil is saturated with either chlorine or hydrochloric acid gas, both gases being soluble to a large extent, especially the hydrochloric acid gas. The temperature of the oil should be maintained as low as possible during the passage of the gas, in order to increase the solubility of the gas. The oxide of the metal, supposing it to be aluminium oxide, $Al_2O_3$, of which the chloride is desired, is introduced into large earthenware retorts provided with a tubulus, and raised to a red heat by means of a charcoal furnace. An apparatus containing the saturated petroleum is now connected with the tubulus of the retort, and sufficient heat applied to raise the oil in vapour. When this comes in contact with the ignited oxide a strong reaction at once commences, fumes of aluminium chloride are at once evolved, and distil over into a receiver placed for their reception; the reaction being maintained as long as any alumina remains in the retort, which may be easily ascertained when no white vapours of aluminium chloride appear in the receiver. A second quantity of ignited alumina is similarly introduced through the tubulus of the retort, and the action maintained as before. Several pounds of alumina may by this means, in a short time, be converted into aluminium chloride, and may be readily purified from any oil which may contaminate it by the application of a gentle heat: metallic bromides may be also readily obtained by introducing bromine in the place of chlorine. I have also used naphthaline chloride with advantage, as also chloride of carbon, but the high price of both render them absolutely unfit as commercial products when compared with rock oil.

## THE WELSBACH INCANDESCENT GAS LIGHT.

*Complete Specification* (A.D. 1885.—No. 15,286).
*Manufacture of an Illuminant Appliance for Gas and other Burners.*

My invention relates to the manufacture of an illuminant appliance in the form of a cap or hood to be rendered incandescent by gas and other burners so as to enhance their illuminating power. For this purpose I employ a compound of oxide of lanthanum and zirconium, or of these with oxide of yttrium, which substances in a finely divided condition when they are heated by a flame give out a full, large, almost pure white light, without becoming volatilised or producing scale or ash, even after being kept incandescent for many hours, but remain efficient without deterioration even when they are long exposed to the air.

The proportions in which the substances are compounded may be varied within certain limits. I have found the following proportions very suitable:—

60 per cent zirconia or oxide of zirconium,
20 per cent oxide of lanthanum,
20 per cent oxide of yttrium.

The oxide of yttrium may be dispensed with, the composition being then—

50 per cent zirconia,
50 per cent oxide of lanthanum.

Instead of using the oxide of yttrium, ytterite earth, and instead of oxide of lanthanum, cerite earth containing no didymium, and but little cerium, may be employed.

For applying the substances mentioned as an illuminant I use a fine fabric, preferably of cotton previously cleansed by washing with hydrochloric acid. I saturate this fabric with an aqueous solution of nitrate or acetate of the oxides, and gently press it until it does not readily yield fluid, so that in stretching or opening out the fabric the fluid does not fill up its meshes. The fabric is then exposed to ammonia gas, and when it has been dried it is cut into strips and folded into plaits. One method of giving the desired shape to the cap or hood is to draw a fine platina wire through the meshes of the net and bend it to the form of a ring so as to give the fabric the shape of a tube, the edges of which are then sewn together with an impregnated thread. The cap or hood thus formed can be supported on cross wires in the chimney of the lamp. The platina wire ring may be attached to a somewhat stronger platina wire to form a supporting stem by which the net can be secured to a holder on the burner tube, the net itself being at such a height that the platina ring is an inch or more above the burner.

On igniting the flame the fabric is quickly reduced to ashes, the residuum of earthy matters nevertheless retaining the form of a cap or hood.

For part of the zirconia a mixture of magnesia and zirconia may be employed with a little loss of intensity of the light.

Obviously fabrics of various forms or constructions may be employed according to the character of burner to which they are applied.

In order to protect the fabric and prevent its rupture when it is exposed to a strong current of gas, stronger threads can be added to the fabric before it is converted into ashes. Also the fabric can be painted with or dipped into concentrated solution of the salts so as to provide a fresh layer of the metallic salts, which becomes fully oxidised soon after the fabric has become incandescent. In order to strengthen the connection of the cone of earths to the platinum wire, those parts of the fabric which are next the wire are more fully impregnated with the solution, or with a solution of about equal parts of nitrates of magnesium and aluminium.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is—

The manufacture substantially as herein described, of an illuminant appliance for gas and other burners, consisting of a cap or hood made of fabric impregnated with the substances mentioned and treated as set forth.

*Complete Specification* (A.D. 1886.—No. 3592).
*Improvements in Illuminant Appliances for Burners.*

In the Specification No. 15,286 of 1885 of Carl Auer von Welsbach is described the manufacture of illuminant appliance for burners, in the form of a cap or hood made by impregnating fabric with solutions of salts of certain rare metals and then by the heat of the flame consuming the fabric so that the skeleton remains consisting mostly of the oxides of the metals, which, heated to incandescence, gives out a brilliant light. The said Carl Auer von Welsbach, continuing his researches since filing the provisional specification No. 15,286 of 1885, has found that certain substances other than those mentioned therein can be advantageously employed in producing such illuminant appliances, and has communicated the present invention, which I will proceed to describe. For making an illuminant cap or hood to produce, when heated, a white light, the following substances may be used:—

1. Pure thorinum oxide makes a hood which is rigid when incandescent.

2. A mixture of thorinum oxide about 3 parts with 2 parts of magnesia makes a hood which is flexible when incandescent.

3. A mixture of thorinum oxide, zirconium oxide, and

yttrium oxide, in nearly equal proportions, gives a slightly yellow tint to the white light.

4. A mixture of thorinum oxide, zirconium oxide, and lanthanum oxide, in nearly equal proportions, the lanthanum a little in excess, gives a very brilliant light, and the hood is flexible when incandescent.

5. A mixture of thorinum oxide and lanthanum oxide in equal parts, with about half a part of magnesia, makes a hood which is flexible when incandescent.

6. A mixture of thorinum oxide about 3 parts with 1 of magnesia and 1 of alumina gives a hood which is very flexible when incandescent.

In the mixtures which include lanthanum oxide, for a portion of that substance yttrium oxide may be substituted.

When a yellow light is desired the mixture may be—

7. Thorinum oxide and lanthanum oxide in equal proportions.

For an orange light it may be—

8. Thorinum oxide and neodymium oxide in equal proportions. As the name neodymium is new it is necessary to explain that it is one of two metals constituting what is generally supposed to be a simple metal, didymium.

For a greenish light it may be—

9. Thorinum oxide and erbium oxide in equal proportions.

In the mixtures 7, 8, and 9, zirconium oxide may be substituted for a portion of the thorinum oxide. Though magnesia and alumina can be employed, as in 5 or 6, it is better to avoid the use of much of these substances, as hoods containing them are not so durable as those from which they are absent.

For impregnating the fabric, solutions of the salts of the metals are employed as described in the previous specification, but it is not necessary that all the substances should be in solution. Some of the salts in pulverulent amorphous or finely crystalline condition may be mixed with a solution of salts of the other metals so as to produce a thickish liquid in which the undissolved salt is suspended. With this liquid the fabric can be repeatedly soaked, surplus liquid being pressed out between the successive impregnations until there is uniform distribution of the substances over the fabric.

In preparing the solutions a number of different salts may be employed. Nitrates are generally soluble; so also, but in less degree, are the sulphates, chlorides, iodides, bromides; also some organic salts, such as acetates or formiates. Generally the fluorides, carbonates, hydroxides, and many of the organic salts are insoluble, or soluble with difficulty. Those products which are insoluble or only partially soluble may, however, be employed as above described, in admixture with solutions of soluble salts.

When the fabric has been thoroughly impregnated and dried, and formed into the desired hood shape, it is not necessary to treat it with ammonia as described in the former specification; it may at once be subjected to the action of heat, care being taken to apply the heat first to its upper part, and then gradually downwards, as may be done by lowering the burner flame within the hood or raising the hood. It is of advantage to strengthen the hood by drawing through it in various directions stronger threads, themselves impregnated with the illuminant substance, or fine platinum wires may be used. The hoods may be made as tubes, woven or knitted, some parts, especially the upper parts, being made stronger by using in these parts meshes of smaller size than the meshes generally, or by double weaving or knitting of the parts that require greater strength. Also the hood may consist of several thicknesses of fine open fabric, or of a single fabric pleated or folded; or, instead of using fabric, a number of separate impregnated threads may be hung from a ring of platinum wire so as to surround the flame. The attachment of the hood or threads to the suspending ring should be strengthened by serving the upper part before burning with a mixture of nitrates of the metals employed and magnesium nitrate. Usually the hood is protected by being enclosed within a glass chimney like that of an argand lamp, but when a chimney is not used it may be surrounded by a cage of fine platinum wire.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is—

In hoods prepared as illuminant appliances for burners, the use of oxide of thorinum alone or in admixture with oxides of zirconium, lanthanum, yttrium, neodymium, erbium, magnesium, or aluminium, substantially as herein described.

*Complete Specification* (A.D. 1886.—No. 9806).

*Method of obtaining Compounds of the Rarer Metals from their Earths for Use as Incandescence Bodies for Illuminating Purposes.*

This invention relates to the treatment of the earths of the rarer metals, such as minerals containing cerium, didymium, lanthanum, thorinum, and zirconium, in order to obtain therefrom solutions suitable for the production of incandescence bodies such as are described in the Specifications to Patents Nos. 15,286 of 1885 and 3592 of 1886.

In treating cerite, orthite, and other similar minerals containing cerium, didymium, and lanthanum, for obtaining these in a separated condition, the minerals are in the first instance heated to a red heat, with free admission of air in those cases in which iron is contained therein in the form of protoxide, in order to oxidise the iron of the cerite compounds to a higher degree, and thus avoid various difficulties in the subsequent operations. This heating process is, however, only applicable when the percentage of cerium compounds is considerable, and when the mineral is a silicate, and not fusible in ordinary temperatures. A number of such minerals comply with these conditions; in particular may be mentioned cerite, the treatment of which will now be described by way of example.

The raw material, as extracted from the earth, is heated to a red-heat in lumps about the size of a fist, with free admission of air, for about an hour.

The mineral is thereby changed in such manner that its original reddish grey colour has been converted into yellow, and that it has taken up oxygen. The lumps, while hot, are plunged rapidly into water, whereby they crumble to pieces, thus greatly facilitating the following disintegrating process in which the material is crushed partly to powder and partly into small particles of about the size of hemp-seed. The finer particles being separated from the coarser ones, both parts are stirred in suitable vessels together with ordinary concentrated hydrochloric acid, whereby the finer particles become decomposed under evolution of heat, while the coarser particles only become slightly heated. After some days the finer particles will be entirely decomposed, and if the proper proportion of acid has been used this will have become entirely exhausted.

The decomposition of the coarser particles takes place more slowly, and is only completed in about a fortnight. It is advantageous to draw off the lye formed after a few days, to levigate the sludge with water, and to mix it with a fresh supply of concentrated hydrochloric acid until all particles susceptible of decomposition are decomposed, which can be ascertained by the fact that the original grains of cerite will have been converted into a friable skeleton mass of silicic acid. The chloride solution obtained by the above process is precipitated by means of oxalic acid, and the oxalates are washed by decantation and through a filter-cloth, and after being pressed dry they are heated to a red heat in shallow iron pans, but only to such an extent that no complete conversion into the oxides is effected.

The brown oxides, containing a considerable amount of carbonic acid, should, on being treated in the cold with

concentrated nitric acid, dissolve after a short time, with ebullition, into a dark red liquid. Only when obtained in the above-described manner is the preparation suitable for the following separation process.

The oxides are now stirred together with water in a fire-clay vessel and heated on a steam-bath, nitric acid being added in small quantities until a frothing is observed to take place after every addition.

As the composition of the minerals is very variable, even when taken from one and the same locality, the quantity of nitric acid cannot be fixed in advance.

The nitrate solution formed after the addition of the nitric acid is digested with excess of the earths. If, after about ten hours digesting, it is not converted into a very fine yellowish red or yellowish powder, but remains of a brown colour, nitric acid must again be added, and this process must be continued until the precipitate shows the above-mentioned colour. The supernatant lye is then of an amethyst colour, and the precipitate formed is insoluble even in very dilute lye.

If, in carrying out the process, so much nitric acid has been added that the yellowish white precipitate is dissolved into a yellowish liquid on the addition of a large quantity of water, then too much acid has been added, and quantities of the earthy sludge, obtained as above described, mixed with water, must be added until the precipitate obtained has the above-mentioned properties.

In this precipitate will be contained the whole of the cerium of the original mineral in the form of a compound insoluble in water, while the lye will contain all the other rare earths.

The cerium precipitate obtained, after washing, is readily soluble in nitric acid when heated, and the dark red solution thus obtained is mainly cerium nitrate.

The principal constituents of the lye will be the elements of didymium (praseodymium and neodymium), and lanthanum.

For separating these from each other, the lye separated from the precipitate is evaporated and treated with nitric acid and ammonium nitrate, and is separated into its constituents by the formation of the ammonium double nitrates.

In order to perfectly separate the lanthanum by means of fractional crystallisation the crystallising process must be repeated several times.

The colourless crystals of lanthanum ammonium nitrate are chemically pure, and form as solution one of the principal ingredients of the liquid for producing the incandescence bodies.

In treating zirconium this is reduced to about the size of peas, heated to a white heat under free admission of air, pulverised, and levigated, and is then digested for several days with concentrated pure hydrochloric acid, for the purpose of removing all traces of iron. The original brownish grey powder is by this means converted into a perfectly white powder, and many of the impurities originally contained in the zirconium crystals are dissolved. The fine zirconium powder is then washed and dried, and is mixed with double the quantity of calcined carbonate of soda, and, after being ground fine, it is subjected to a white heat for about three hours in a platinum crucible. The cakes of soda melt thus obtained are placed in cold clean water, when a fine white powder will be precipitated, while numerous bodies that are not useful for the purposes of the invention pass into the mother-liquor. The white powder is washed in water, dried, and treated with sulphuric acid under trituration until a sample heated on platinum clearly shows an excess of sulphuric acid.

The decomposition of the white powder by sulphuric acid takes place under considerable heating, and care must be taken that the acid is very gradually added (the powder remaining perfectly dry), as otherwise a scattering of the mass will ensue. The powder is then heated to the boiling-point of the sulphuric acid, whereby the greater part of the excess of acid will be driven off. After cooling, the powder is mixed with a large quantity of cold water under stirring, whereby the zirconium will be dissolved as sulphate, together with other bodies. The undissolved precipitate is unconverted zirconium and silicic acid. This is separated by filtration and washed.

The before-mentioned solution of zirconium sulphate is precipitated by ammonia in the cold, and is washed. If this material be now dissolved in nitric acid, so that no considerable excess of acid occurs, a brilliant white powder will after a short time be precipitated, which is a peculiar combination of zirconium, containing this metal in an almost chemically pure condition. The impurities, such as iron, alumina, &c., remain in the lye. This reaction is based on the fact that a small quantity of sulphate of ammonia present in a solution of nitrate of zirconium effects the separation of the before-mentioned compound, completely so when heated, and partially when cold. As an excess of sulphate of ammonia dissolves the zirconium precipitate, this is to be avoided.

The precipitate containing the zirconium is almost quite insoluble in water, but soluble in nitric acid when freshly precipitated; when digested with ammonia it is rapidly converted into dense zirconium hydroxide, which is readily separated by washing. This body is then dissolved in concentrated nitric acid, and the solution is evaporated on a water-bath, producing clear gum-like crusts consisting of zirconium nitrate.

This substance dissolved in water forms a second main constituent of the incandescence body.

The presence of small quantities of iron, such as are contained in the preparation of zirconium heretofore made, is very detrimental to the action of the incandescence body.

Having now particularly described and ascertained the nature of my said invention, and in what manner the same is to be performed, I declare that what I claim is—

1. The method substantially as herein described of treating cerite, orthite, and similar minerals containing cerium, didymium, and lanthanum, with hydrochloric acid in the cold, for effecting the separation of the said metals.

2. The method substantially as herein described of separating the cerium from the minerals referred to in the preceding claim, by treating the chloride solutions thereof with oxalic acid, heating the oxalates obtained to redness, and treating the resulting oxides with nitric acid, whereby the cerium is obtained in the form of a nitrate solution.

3. In combination with the method for the separation of cerium from minerals containing cerium, didymium, and lanthanum, referred to in the preceding claim, the separation of the didymium and lanthanum contained in the lye after separation of the cerium, by evaporating the lye, and treating the residue with nitric acid and ammonium nitrate, whereby ammonium double nitrates of the said metals are obtained in the form of crystals, substantially as herein described.

4. The method substantially as herein described of treating zirconium for the removal of all traces of iron therefrom, consisting in first heating the zirconium to a white heat under free admission of air, and then, after finely pulverising the same, treating it for several days with hydrochloric acid.

5. The method substantially as herein described of producing zirconium in a form suitable for an incandescence body, by first converting the zirconium into a sulphate, and, after treating with ammonia, dissolving the same in nitric acid, thereby obtaining a precipitate which, when digested with ammonia and dissolved in nitric acid and evaporated, produces zirconium nitrate.

6. The method substantially as herein described of separating a zirconium compound from a solution of zirconium in nitric acid by means of sulphate of ammonia, whether this be present in the solution from previous processes or be subsequently added.

# THE HARDNESS OF METALS.*

By THOMAS TURNER, Assoc. R.S.M., F.C.S.,
Lecturer on Metallurgy, Mason College, Birmingham.

(Continued from p. 182.)

## Part II.

Reference has been made to Moh's scale of hardness commonly used by mineralogists. In spite of its great usefulness as a ready means of classification, it possesses imperfections which have long been recognised, and many attempts have been made to remedy these. One of the most successful and accurate of these attempts is represented by the sclerometer, which appears to have been first used in Germany in 1883, by Seebeck, in a study of the hardness of calc spar and gypsum. His results were published in the "Programm des Berlinischen Real gymnasium," his conclusion being that the hardness of gypsum was the same in all directions on the same face of the crystal, while that of calcite varied according to the angle at which the crystal was examined.

The subject was afterwards more completely examined by Franz, in 1850 (*Pogg. Ann.*, lxxx., p. 37), which is the earliest paper on the subject to which I have access. The apparatus itself, which is figured in the original paper, practically consisted of a diamond or steel point, balanced at the end of a beam, and upon which, by means of a small table, any desired weight could be placed. The specimen to be examined was fixed in a revolving table underneath the point, and the weight was gradually increased until a visible scratch was produced on drawing the crystal under the weighted point. Franz concluded that the hardness of a crystal was greatest in the direction of cleavage, and least in a direction at right angles to this. His average results are as follows:—

| Crystal. | Moh's Scale. | Weight in Grammes. Steel Point. | Diamond. |
|---|---|---|---|
| Gypsum .. .. | 1·5 | 1·5 | — |
| Calcite .. .. | 3 | 9 | — |
| Fluor-spar .. .. | 4 | 36 | — |
| Dioptase .. .. | 5 | 115 | — |
| Apatite .. .. | 5 | 163 | 12 |
| Diopside .. .. | 5—6 | 205 | — |
| Felspar .. .. | 6 | 260 | 20 |
| Pistazite .. .. | 6—7 | — | 24 |
| Quartz .. .. | 7 | — | 34 |
| Zircon .. .. | 7·5 | — | 38·5 |
| Tourmaline .. .. | 7—7·5 | — | 39·5 |
| Beryl .. .. | 7·5—8 | — | 43 |
| Topaz .. .. | 8 | — | 43 |
| Sapphire .. .. | 9 | — | 51 |

It will be seen from the above table that with soft minerals Franz employed a steel point, while for hard minerals the diamond was used. The values obtained agree very closely indeed with what might be anticipated from Moh's scale, and in this respect form a striking contrast with some other forms of apparatus previously described.

Since the experiments of Seebeck and Franz the sclerometer has been used by a number of observers, though its application appears to have been almost entirely confined to Germany. Recently an important modification has been introduced by Pfaff,† who draws a weighted diamond a definite number of times over the surface of the crystal to be examined, and weighs the specimen before and after the experiment. From the loss of weight and the known density of the material the depth of the grooves can be calculated, and Pfaff states that the hardness varies inversely as the depth of the groove. (*München Ber.*, 1883, pp. 55, 372; 1884, p. 255, more readily accessible as abstracts. *Neues Jahrb. f. Mineral*, 1884, ii., p. 4. *Beiblätter*, 1884, p. 278; 1885, p. 82). This method was used for gypsum, calc spar, and other soft minerals, for which it appears to be specially suited. I believe the results obtained by such a method would correctly indicate hardness if the precaution be taken only to remove the mineral in the form of very fine powder. If, however, sufficient pressure were applied to remove definite shavings or cuttings of the material then tenacity would interfere. The use of a diamond cutter in this manner is not admissible, however, in the case of soft metals; for while the diamond will cut the hardest hardened steel freely, it will not remove a cut from annealed steel or iron, or other soft metals, owing to the material clinging tenaciously and dragging under the treatment (G. Jones, *The Engineer*, lxii., p. 426). This method not being suitable for hard minerals, Pfaff adopted another system in such cases, the principle of which had already been applied by Bottone. A weighted diamond-borer was caused to rotate a given number of times, the depth to which it penetrated being measured by an ingenious lever indicator. The depth of the hole varies inversely as the mean hardness of the crystal. Though it appears to be extremely difficult to suggest a method of determining the mean hardness of a mineral, which should be open to less objection than that just described, still it may be pointed out that it is by no means perfect. As has been previously shown, if cuttings of any considerable magnitude were taken then the tenacity of the substance would have an important influence; further, in cases where marked plasticity was possessed this would introduce some error, while if the hole were not kept constantly clear of turnings a considerable amount of force might be expended on merely grinding these to powder.

The various methods employed for the determination of hardness by the mineralogists have been treated at somewhat considerable length, partly with the object of showing the methods we have at our disposal, and partly because the instrument I have employed is in reality only a modification of that originally described by Seebeck, and used by Franz over thirty years ago. My apparatus was constructed for use with cast-iron, but it has since been applied to a number of other substances.

Hitherto there have been few accurate observations of of the hardness of iron and steel. The workman judges of this character by the facility with which the iron can be drilled, turned, or filed, the hardest metal producing most sound, and yielding the smallest quantity of turnings or filings when worked. Such observations are of course only qualitative. The earliest attempt to give a quantitative value to hardness tests is represented by the work of the American experimenters to which reference was made (p. 180). Their method depended upon the production of a measurable indentation by means of a weighted punch, and the objections to such a system have been already mentioned. Doubtless the results obtained were of practical value, but they did not accurately represent the hardness of the metal. Two other methods depending upon similar principles have quite recently been brought under my notice.

1. Mr. G. A. A. Middleberg, of Amsterdam, writes to *Engineering*, 1886, ii., p. 481, as follows:—

"For many years I have used the following apparatus to ascertain the relative hardness of railway tyres, &c., and I find that it gives accurate and satisfactory results:—

A knife, *a* (see sketch), of hardened steel ¾ in. long with curved edge is pressed by lever and weight, *b*, on the surface of the metal, leaving there a line of a certain length, proportionate to the hardness of the metal. The range of the impression is about $\frac{1}{16}$ in. for copper and $\frac{1}{64}$ in. for hardened steel, and may be accurately measured. For softer metals a lighter weight, *b*, might be chosen."

The practical value of such observations for certain purposes cannot be doubted, but it will be seen that any such apparatus must fail to give accurate values for true hardness. Obviously with two samples of equal hardness, but differing in tenacity, a deeper indentation would be made in the less tenacious metal.

* Read before the Birmingham Philosophical Society, Dec. 9, 1886.

† I regret to learn, from Mr. Brough, that Mr. Pfaff has died since the above was written.

2. The following method has been communicated to me by Mr. Keep, of the Michigan Stove Company, Detroit, and from the tone of Mr. Keep's letter I conclude he would have no objection to my using the information it contained. A steel head half-an-inch in square section was prepared, and carefully divided into 100 pyramids, each as nearly alike and as sharp as possible. The head was attached to a bar arranged to move easily and accurately by means of guides. The test piece was prepared by grinding its sides as nearly parallel and as smooth as possible. It was then arranged in such a manner that only a corner point of the tool rested on the prepared surface, and so that when one row of points had left its mark the next row just began to act. The tool was pressed on the metal by means of a swinging weight of 25 lbs., which was allowed to fall one inch. The number of marks produced was then counted by means of a lens, while a light streamed across the surface. This method is very ingenious, but was not found to be very satisfactory. In some cases with iron, and especially with brass and copper, the whole surface was depressed instead of small indentations being produced. Mr. Keep also states that the number of marks does not vary as the force employed. Other objections will suggest themselves.

I have previously shown that hardness and tenacity are distinct physical properties, and that methods depending on the production of indentations or the use of cutting tools fail, at least in some measure, to distinguish between these two properties. It therefore becomes of interest to enquire what form of experiment is most likely to yield accurate results.

Theoretically, hardness is measured by the force necessary to separate the smallest particles or molecules of the substance, as distinct from tenacity, which is measured by the force necessary to separate the aggregated molecules, or the mass as a whole. Hence hardness is just overcome when abrasion begins, and can be accurately measured if the force necessary to produce abrasion is determined. In the use of cutting instruments the results become less and less accurate expressions of hardness as the thickness of the turnings increases, and hence the methods employed by Pfaff only yield correct results when indefinitely small portions of the material are removed at each operation. Theoretically, therefore, the best method is to determine the force necessary to just produce an abrasion with a tool of a given size and shape; while practically this becomes a point to which a given force is applied. This method, however, though theoretically the most perfect, possesses an inherent difficulty, owing to the uncertainty as to the moment at which abrasion commences.

In connection with the subject of abrasion, Professor R. H. Smith, of Mason College, allows me to mention a method adopted in his laboratory, some time ago, for the examination of the effect of tempering on the hardness of steel. The specimen to be tested was first carefully weighed, and then pressed with a definite force against a revolving grindstone or emery wheel, the number of rotations of which was observed. In using an emery wheel sufficient water was made to flow over the specimen to prevent any considerable rise of temperature. The loss of weight of the specimen at the end of the experiment gave an indication of the hardness of the metal. It will be seen that the material is removed by means of abrasion, and hence the method is, in this respect, superior to those previously mentioned. I am, however, unaware how far results obtained in this manner agree with those given by other forms of experiment. But such a method is only suitable for hard substances, for, as pointed out by Gavin Jones (*Engineer*, lxii., 426), emery wheels, especially in dry grinding, will grind hardened steel freely, but will scarcely act on soft steel or iron, much less on copper. The hardened steel cuts with a crisp feel under the emery wheel, whereas the softer metals cling tenaciously and drag under the treatment, the particles yielding slowly, and being torn off with great force rather than cut.

My own original apparatus consisted merely of a balanced lath, capable of motion in a horizontal plane. Through one end of the lath, at right angles to its length, passed a cutting diamond, arranged so that it could be weighted as necessary. The weighted diamond point was drawn over the smooth surface of the metal to be tested, while the weight necessary to produce a visible scratch was observed; the weights were then diminished until no scratch was visible on again drawing the diamond over the metallic surface. The mean of these observations was taken as the measure of relative hardness. The results are given in Table B, and will be again referred to. It will be sufficient now to say that the values obtained with this simple apparatus agree closely with those afterwards obtained in similar experiments with a more perfect instrument and another diamond. Further, I have recently tested the specimen containing 2 per cent of silicon with my newest apparatus, and obtained a hardness of 21, as against 22 with the same specimen and my first arrangement.

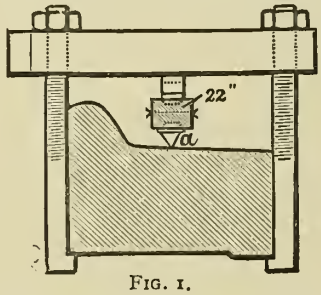


Fig. 1.

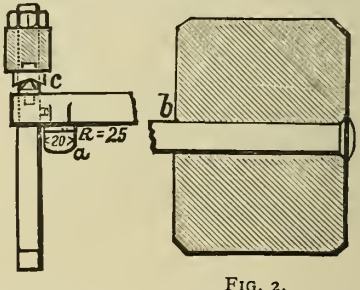


Fig. 2.

(To be continued).

## THE ROYAL JUBILEE EXHIBITION, MANCHESTER.

The first Industrial Exhibition which has ever been held in Manchester promises, from the advanced state of preparation in which it now is, to satisfy the hopes of the most sanguine of its promoters. The general object and scope of the Exhibition will be to illustrate, as fully as possible, the progress made in the development of arts and manufactures during the Victorian era. The principal sections into which it is divided are—Industrial Design; Machinery and Engineering Plant, &c.; Chemical and Allied Industries; Electric Light, &c.

The Chemical Section is very well illustrated, and occupies the chief portion of the south of the main building, covering a space of 700 ft. × 60 ft. It is subdivided into fifteen groups, besides a special Sub-section which is devoted to Photography, an art which is essentially a product of the Victorian era, the whole of its history being comprised within that period. The first exhibits which

catch the eye on entering the Chemical Section are those of Messrs. Bailey and Co., of Salford, and Messrs. Doulton and Co., of Lambeth, both of whom make a good show of the appliances and apparatus for which they are each celebrated. A few yards further along we note a new instrument invented by Mr. J. W. Lovibond, called the Tintometer: by its means the depth of colour in liquids, and even solids, can be accurately measured in degrees, and placed in their position in a colour-scale. The instrument consists of two tubes, 18 inches long, side by side, open at the ends. In one tube is placed the liquid to be examined, and in the other a series of coloured glasses with which the comparison is to be made: both these tubes are observed through a single eyepiece. The standard scale of colour is formed of a series of glasses, of various known tints and depth of colour, all having a certain proportion to each other. It can be easily seen that when once the colour of any solution has been ascertained, a record can be kept, and the same shade reproduced at any time for comparison.

The Harden Star and Sinclair Fire Appliance Company, Limited, show a general assortment of fire appliances, including hand fire grenades, automatic sprinklers, &c. The new light known by the name of Lucigen is also exhibited by this firm. The light, which is an exceedingly powerful and at the same time mellow one, is produced by burning creosote, tar oil, or other heavy hydrocarbon, in a special burner, by means of compressed air. The action of the compressed air is to form the oil into an extremely fine spray, and in this condition it is burnt, giving off no smoke or smell. It is claimed for this light that it will burn equally well in the wind and rain, and requires no lantern.

Otto Wolters shows an assortment of assay, chemical, and bullion balances, including his improved short-beamed analytical balances. A very good collection of theodolites, anemometers, levels, pressure and vacuum gauges, thermometers, &c., is shown by J. Casartelli, of Manchester.

Messrs. Mottershead and Co. exhibit a complete set of chemical and physical apparatus for private laboratories, schools, &c., as well as fine chemicals for use in medicine and the arts, peptonised foods, &c.

Plant for bleaching cotton, linen, &c., by the Blanchine process, which dispenses with the use of lime, and samples of cloth that have been so bleached and afterwards dyed, are shown by the East Lancashire Chemical Company.

The British Alizarine Company, Limited, have a very good case of anthracene derivatives, such as alizarine, anthro-purpurin, and flavo-purpurin, employed in the dyeing and printing of cotton and woollen fabrics, and specimens illustrating the various stages of the manufacture of these products.

Amongst the exhibits of Chemical Research are the cases of Sir Henry Roscoe, M.P., containing a collection of pure vanadium and tungsten, with compounds of those rare metals; that of Edward Schunck, Esq., F.R.S., who exhibits a complete collection illustrative of his researches on the principles contained in madder, constituents of natural indigo, &c.; and lastly, that of Dr. W. H. Perkin, F.R.S., who exhibits specimens illustrating his discovery of the first coal-tar colour,—mauve,—which was the commencement of the now important coal-tar colour industry. Some of the most interesting specimens are those of mauve, as first made in 1858; para-saffranine, as first obtained by oxidising mauveine; coumarin, the odoriferous principle of the Tonka bean; cinnamic acid, and others,—all first prepared artificially by Dr. Perkin.

Messrs. Hardman and Co. show a model of the plant required in the manufacture of some of the useful products from residuals obtained in the manufacture of coal-gas. The specimens include crude and purified products obtained from coal-tar, ammoniacal liquid, and spent oxide.

There is a good collection of pigments, paints, &c., among which we may mention the exhibit of Wm. Pakeman and Co., of colours for calico-printers, paper-stainers, printers, &c., all free from arsenic, and that of Wm. Taylor and Co., Limited. A novelty in the way of paint, is that exhibited by Mr. Henry Crookes, called Heat-Indicating Paint, from its property of changing from a bright red to a dark brown colour when heated up to 140° F., and resuming its original colour on cooling; this property renders it very useful to engineers and others for showing the temperature of bearings or other surfaces liable to be overheated. One of the most important improvements in paint making within the last few years is that of Messrs. J. B. Freeman and Co., who exhibit their non-poisonous white-lead; all who have had experience of domestic painting will appreciate such an improvement as the use of this will be. It is entirely free from smell and perfectly harmless to the workmen in all stages of its use and manufacture; it is not darkened by sulphuretted hydrogen, which is another great advantage in this country. The basis of this paint is sulphate of lead, but it is prepared in such a manner that its character is quite changed; it is no longer "slimy," when mixed with oil, and possesses great density and opacity, while its whiteness is greater than that of the finest white-lead made by the Dutch process.

The Select Exhibit of the Committee of Section III., collected by Mr. Watson Smith, is of extreme interest, comprising the MSS. and Relics of Dr. John Dalton, the propounder of the atomic theory, Sir Humphry Davy's chemical balance, &c. Specimens of American and Russian petroleums, also of crude anthracene obtained by passing Russian petroleum residues through red-hot tubes. A parti-coloured flag, showing the exact amount of dyeing power in one pound of Manchester gas coal. Specimens of raw jute fibres, cottons, barks, resins, and many others, illustrating a large number of important industries.

Group VI. comprises fine chemicals, alkaloids, extracts, &c., the principal exhibitors being James Woolley and Sons, Grimshaw Bros., Howards and Sons., and Kay Bros.

In the Metallurgical Group Messrs. Henry Wiggin and Co. exhibit specimens of nickel and cobalt ores, and materials showing the process of manufacture from the native mineral to the finished article.

The Cowles Electric Smelting and Aluminium Co. show sample ingots of the products of the electric smelting furnace, and Cowles process of manufacturing metallic aluminium.

Messrs. Peter Spence and Sons show the largest crystal of alum ever made; it is about 6 feet in diameter and 12 feet high and of the finest quality. They also show many other specimens of alums and compounds of alumina used by paper makers and dyers.

The Sub-section of Photography is of great interest, containing specimens of photographs obtained by all the known methods. An enlarged copy of a photograph of the great nebula in Orion, taken by A. A. Common, Esq., and a collection of astronomical photographs taken by MM. Henry Paul and Prosper at the Paris Observatory, are specially interesting.

The Irish section contains a collection of scientific apparatus exhibited by G. F. Fitzgerald, Esq., comprising the late Dr. Lloyd's apparatus for exhibiting conical refraction. A model illustrating the electro-magnetic and luminous properties of the ether, and others.

Messrs. Yates and Sons show an optical bench and other optical instruments.

But the most important exhibit of scientific instruments in the whole building is undoubtedly that of Mr. Howard Grubb, F.R.S., comprising as it does such a large number of astronomical instruments; among these are two new forms of telescopes as constructed for Dr. Huggins and Mr. J. Roberts; the latter carrying an 8-inch refractor for general micrometrical work, and a 17-inch reflector especially fitted for steller photography; a new form of binocular telescope, by which means any size telescope can be used as binoculars, instead of as formerly the size

being limited by the distance between the human eyes; models of the great Vienna Equatorial, and of a design for the Lick Observatory, California, all the motions of which are to be worked by electricity; Microscopes, spectroscopes, and many other instruments, too numerous to detail.

The other sections of this Exhibition, which we may call the unscientific sections, are equally, and perhaps to many people more interesting, and we can only hope that a complete success will reward the labours of the Committees to whom the organisation has been entrusted.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, April 21st, 1887.*

Mr. William Crookes, F.R.S., President, in the Chair.

Mr. T. H. Redwood was admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Ernest Francis Ehrhardt, B.Sc., Hillcrest, Richmond Hill Road, Edgbaston; Henry Hewetson McMinnes, Agricultural College, Roseworthy, Adelaide, South Australia; John William Young, B.A., Guilford Lodge, Brentwood.

The following were elected Fellows of the Society:—Messrs. W. C. T. Beasley; Edward R. Blundstone, B.A.; Samuel F. Burford; James W. Chenhall; George Collar, B.A.; Henry Danber, jun.; Hugh Gordon; William Gregory; David Lloyd Howard; Edward Rawlins; Louis H. Schubert; Leonard O. Simmons; Samuel Sutcliffe.

The following papers were read:—

37. "*The Atomic Weight of Gold.*" By T. E. Thorpe, F.R.S., and A. P. Laurie, B.A.

Former determinations of the atomic weight of gold have been made by Dalton, Proust, and Oberkampf, in 1806; Berzelius, in 1813; Pelletier, Javal, and again by Berzelius, in 1844; by Levol, in 1850; and Thomsen, in 1876. The numbers obtained differ widely from each other, partly owing to the unstable character of the salts of gold, and partly to imperfect methods of analysis. The number usually accepted is 196·2, being the value obtained by Berzelius in his second series of determinations, from the analysis of the double chloride of gold and potassium. A special reason for undertaking a revision of the atomic weight of gold arises from the circumstance that a higher value than that usually assigned to this element is demanded by the periodic law.

The salt employed by the authors is the bromide of gold and potassium, which crystallises readily from water, and (as proved by a series of analyses of different crystallisations) is stable at ordinary temperatures. The salt was prepared by digesting together gold, water, bromide, and potassium bromide, and was then three times crystallised.

The method of analysis was as follows:—

About 15 grms. of the double salt was introduced into a large porcelain crucible, carefully dried in an air-bath, and then decomposed by heating over a Bunsen flame. The crucible containing the mass of decomposed salt was weighed against a similar and similarly treated crucible, the bromide of potassium washed out with hot water, the solution being drawn into a bottle by reverse filtration, and the gold ignited in a muffle, and again weighed. From these weighings the first set of values for the atomic weight was calculated. A weighed quantity of silver (the purity of which had been tested at the Mint by comparison with the trial plate) was dissolved in dilute nitric acid and added to the potassium bromide, and the excess of the potassium bromide precipitated by a solution of silver nitrate of known strength. From these results the second series of values was calculated. The silver bromide was then collected, dried at 160° C., and weighed. From these weighings a third series of values was calculated.

On comparing the weight of silver used with the weight of bromide of silver obtained, the ratio between them was found to be Ag : AgBr = 1 : 1·74072. According to Marignac, Ag : AgBr = 1 : 74077. According to Stas, Ag : AgBr = 1 : 1·74081. The close agreement of these ratios with that obtained by the authors is a proof of the absence of chlorine in the bromine or potassium bromide employed by them in the formation of the double salt.

The ratios assumed between Ag, Br, K, O, and H were those of Stas and are as follows:—

| | |
|---|---|
| Ag .. .. .. .. | 6·7449 |
| Br .. .. .. .. | 4·99634 |
| K .. .. .. .. | 2·44523 |
| O .. .. .. .. | 1 |
| H .. .. .. .. | 0·06265 |

On the basis of these numbers, the results of the various observations may be thus summarised:—

*Series I.* (8 *Experiments*).

| | |
|---|---|
| Au : KBr .. .. | 37·49137 : 22·61944 |
| „ .. .. | 1·65748 : 1 |
| Au : O .. .. .. | 12·3343 |
| Au : H .. .. | 196 876 |

*Series II.* (9 *Experiments*).

| | |
|---|---|
| Au : Ag .. .. | 41·67403 : 22·79374 |
| „ .. .. | 1·82831 : 1 |
| Au : O .. .. .. | 12·3318 |
| Au : H .. .. | 196·837 |

*Series III.* (8 *Experiments*).

| | |
|---|---|
| Au : AgBr .. .. | 36·50997 : 34·76060 |
| „ .. .. | 1·05033 : 1 |
| Au : O .. .. .. | 12·3322 |
| Au : H .. .. | 196·842 |

On the assumption that these values have equal weight, the final value from the whole 25 experiments becomes—

| | | Diff. from mean. |
|---|---|---|
| Series I... .. | 196·876 | +0·026 |
| „ II... .. | 196·837 | −0·013 |
| „ III... .. | 196·842 | −0·008 |
| Mean .. | 196·850 | |

When a considerable portion of the determinative work connected with this investigation had been accomplished, a paper on the same subject appeared in the *Berichte* for February, 1887, by Krüss. Krüss also used potassium bromanurate, but his method of treating the salt differed somewhat from our. The following table contains a summary of his results:—

| | Au (H=1). |
|---|---|
| I. Au : $KBr,Br_3$ (9 experiments) .. | 196·741 |
| II. Au : $Br_4$ (5 experiments) .. .. | 196·743 |
| III. Au : $Br_3$ (4 „ ) .. .. | 196·619 |
| IV. Au : KBr (4 experiments) .. .. | 196·620 |

He also analysed a neutral solution of auric chloride, obtaining the value Au = 196·594.

He adopts as the most probable value Au = 196·64.

### Discussion.

The President, after referring to the great value of such investigations, said that he should have been glad to have heard more from the authors regarding their method of weighing, and of the means they had adopted to control the accuracy of their weights, and to correct for the buoyant effect of the air; the errors incidental to the operations of weighing were often greater than the minute errors involved in the chemical operations. The quantities

of material used in the various experiments appeared to him to be very small: nevertheless the agreement between the results of the several experiments was highly remarkable.

Professor THORPE, in reply, said that they had endeavoured to eliminate the corrections necessary on account of buoyancy, and of changes due to deposition of films of moisture, &c., by always using as a tare to the apparatus weighed a precisely similar apparatus which had been treated in the same way. The argument that the same result would have been obtained by means of a single experiment by taking the aggregate amount of salt used in all the experiments together presupposed that the errors of a series of experiments were all in one direction; but this was not the case.

38. "*The Atomic Weight of Silicon.*" By T. E. THORPE, F.R.S., and J. W. YOUNG, B.A.

The authors have attempted to redetermine the atomic weight of silicon by estimating the quantity of silica yielded by decomposing known weights of silicon tetrabromide by means of water. The results of their experiments are seen in the following table:—

| Wt. of $SiBr_4$ *in vacuo*. | Wt. of $SiO_2$ *in vacuo*. | Si (H=1). |
|---|---|---|
| 9·63007 grms. | 1·67070 grms. | 28·347 |
| 12·36099 | 2·14318 | 28·303 |
| 12 98336 | 2·25244 | 28·347 |
| 9·02269 | 1·56542 | 28·352 |
| 15·38426 | 2·66518 | 28·243 |
| 9·74550 | 1·69020 | 28·325 |
| 6·19159 | 1·07536 | 28·429 |
| 9·51204 | 1·65065 | 28·366 |
| 10·69317 | 1·85555 | 28·364 |

The aggregate weight of the silicon tetrabromide employed in the various experiments was 95·52367 grms.; it yielded 16 56868 grms. silicon dioxide. Assuming with Lother Meyer and Seubert that the most probable ratios for the atomic weights involved in the calculations are —

| | |
|---|---|
| Br .. .. .. .. | 4·99721 |
| O .. .. .. .. | 1 |
| H .. .. .. .. | 0·06265 |

the above numbers give as the atomic weight of silicon 28·332 if H=1.

The previously recorded values are all based upon the ratios of equivalent quantities of silicon tetrachloride, silver, and silver chloride, and were obtained by using comparatively small quantities, *i.e.*, 1 to 2 grms. of the chloride. They are as follows:—

| Date. | Authority. | Method. | No. of Expts. | Si(H=1). |
|---|---|---|---|---|
| 1845.. | Pelouze | $SiCl_4 : Ag$ | 2 | 28·41 |
| 1859.. | Dumas | $SiCl_4 : Ag$ | 2 | 27·99 |
| 1861.. | Schiel | $SiCl_4 : AgCl$ | 2 | 27·99 |

39. "*Note on Substitution in the Benzene Nucleus.*" By H. FORSTER MORLEY.

In an addendum to his paper on "An Explanation of the Laws which govern Substitution in the case of Benzenoid Compounds," Dr. Armstrong says that the formation of metanitro-derivatives on nitration of the sulphates of dimethylaniline, ethylaniline, and ethylpara-toluidine, while aniline and para-acetyltoluidine produced para- or ortho-derivatives, was due to an increase in the basic powers of nitrogen consequent on the introduction of hydrocarbon radicles in place of hydrogen. The experiments quoted admit, however, of a different explanation, those substances which are mentioned as giving meta-derivatives having been nitrated in presence of a large excess of ice-cold sulphuric acid, the others having been nitrated by a different method.

Dr. Armstrong's hypothesis, that meta-substitution is always preceded by combination of the reagent that produces substitution with the radicle already in the benzene nucleus, can hardly be maintained in face of such facts as that strong nitric acid converts dimethylaniline into a paranitro-derivative.

We know nothing concerning the cause of formation of meta-compounds; but only that when the group already present is highly chlorous, the new radicle, on entering, takes up the meta-position.

40. "*Reply to the Foregoing Note.*" By HENRY E. ARMSTRONG.

It is pointed out that Dr. Morley somewhat misrepresents the author's views. In order to make this clear, the formation of ortho- and para-derivatives is more fully discussed, and an explanation is given of the reasons which led him to think it probable that the behaviour of a compound like dimethylaniline would not in all cases be strictly in accordance with the para-ortho law. The author considers that Dr. Morley's statement, that "the group $N(SO_4H)H_3$ in aniline sulphate, &c., is more chlorous than $NH_2$, and hence gives rise to meta-derivatives," is a mere phrase; it in no way follows that such is the case, inasmuch as compounds containing the basic radicle $NH_2$, or allied groups, and those containing the chlorous radicles Cl, Br, &c., in most respects behave alike.

DISCUSSION.

Mr. GROVES, referring to the author's remarks on the action of sulphuric acid on aniline, said that when preparing sulphanilic acid he had been unable to find any intermediate product.

Prof. MELDOLA said that he had repeated many of Nölting and Collins's experiments, and that his results were entirely confirmatory of theirs. In preparing sulphanilic acid on a large scale no intermediate compound was formed, according to his experience.

Dr. MORLEY said that it appeared to him that the cases quoted by Dr. Armstrong did not serve to substantiate his view any more than those previously advanced.

Dr. ARMSTRONG, replying to Mr. Groves, said that it was not to be expected that an intermediate product such as he had referred to would be noticed in preparing sulphanilic acid. As regards Dr. Morley's criticisms, it was most important to elicit opinions on the subject under discussion, and such criticisms were most welcome; but it was clear that Dr. Morley had failed to understand his views.

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At the next meeting, on May 5th, the following papers will be read:—

"A Contribution to the Study of Well Waters," by R. Warington, F.R.S.

"The Influence of Temperature on the Heat of Dissolution of Salts in Water," by Prof. Tilden, F.R.S.

"Crystals in Basic Slag," by J. E. Stead and C. H. Ridsdale.

"The Distribution of Lead in the Brains of Two Factory Operatives Dying Suddenly," by A. Wynter Blyth.

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## PHYSICAL SOCIETY.

*April 23rd, 1887.*

Prof. W. G. ADAMS, Vice-President, in the Chair.

The following papers were read:—

"*On Delicate Calorimetrical Thermometers, and on Expansion of Thermometer Bulbs under Pressure.*" By Prof. PICKERING.

The reading of a delicate mercurial thermometer, when placed in a bath at constant temperature, is found to depend on whether the thermometer was at a higher or lower temperature than the bath before immersion. Capillarity was suggested as an explanation, but experiment showed that the effect was not always greatest at the narrow parts of the tube, and hence this idea was discarded. By using the same tube with different bulbs attached the differences varied, and eventually the effect

was found to be caused by exposing the inside of the tube to air and moisture, for when bulbs were attached to new tubes without being so exposed the differences between the rising and falling readings disappear. Hence, for very delicate thermometers, great care should be taken not to expose the bore of the tube, and calibration of a tube before attaching the bulb must not be attempted. Even in the best tubes, after every possible precaution has been taken, the author finds some parts about which the mercury appears to stick, and in delicate observations these parts of the tube are to be avoided. He also finds it necessary to gently tap the top of the tube to relieve any friction, and has devised a clockwork arrangement for performing the operation uniformly.

In the second part of the paper the author describes the want of concordance between two thermometers which have been compared with the same standard, and finds it due to the expansion of the bulbs not being in all cases proportional to the difference of pressure between the inside and outside. Thermometers with large thin bulbs show greatest discrepancies, and the remedy is found to be in making the bulbs more rigid. This is done by having a double bulb, making them from cylindrical tube instead of by blowing, and increasing the thickness of the walls of the bulb. A knife-edge arrangement in the upper part of a thermometer is described, by which the same part of the graduated tube can be used whatever the temperature (about which small changes are to be observed) may be. The proper amount of the mercury column can be cut off with the greatest nicety by its use.

Mr. Whipple remarked that phenomena similar to those described in the paper were constantly coming under his notice, and mentioned the pressure corrections they were applying to thermometers used *in vacuo*, during some pendulum experiments at present being carried out. He also described the Kew method of determining the pressure correction in deep sea thermometers, which are protected by an outer glass jacket filled with alcohol.

Mr. Lant Carpenter described the first comparison experiments made at sea with protected and unprotected bulb thermometers.

In answer to questions, Prof. Pickering said the range of pressure used was from 0 to 3 atmospheres, and in his most delicate thermometer, where 200 m.m. correspond to 1° C., the difference between readings taken in horizontal and vertical positions amounts to 30 m.m.

"*Note on Magnetisation: on Sequences of Reversals.*" By R. H. M. Bosanquet, M.A.

Some experiments have recently been made on an iron bar whose magnetic properties under reversals with ascending values of current were first determined some years ago. The magnetic resistances have again been determined, first with ascending values of current, and afterwards with descending values. In all cases the induction was measured by reversing the current. The results, generally, show a greater magnetic resistance for descending values of current, except for small inductions, where the resistance was less, when the experiments were performed in the above order. The paper concludes with a molecular hypothesis to explain the above results.

"*On a Thermo-dynamical Relation.*" By Prof. Ramsay and Dr. S. Young.

The paper is an extension of one presented to the Society on Feb. 26, and of which an abstract was read by the secretary. The numerical results are given, from which the authors deduce the relation $p = b\,t = a$ for constant volume is deduced, and additional reasons are given for believing acetic acid (whose vapour density at ordinary temperatures is abnormal) to be a mixture of $C_2H_4O_2$ and $C_4H_8O_4$, the former preponderating as the temperature rises. The authors ask the society for a name to designate lines connecting pressure and temperature at constant volume, and for which they suggested "*isochors*" in their previous paper.

## NOTICES OF BOOKS

*Report of the Chemist to the New York Agricultural Experiment Station.* By S. M. Babcock. Elmira, N.Y.: Advertiser Association. 1887.

The experimental work carried on in the chemical laboratory during the year 1886 has been principally a continuation of the study of milk and butter begun last year, and described in the last Report. A new viscometer has been constructed which promises to be of great assistance, as by its means certain important properties of milk and butter, hitherto unrecognised, can be investigated.

The apparatus used last year was similar in principle to the viscometers used for testing oils, but it was found to be of no good for testing milk, as the small quantities of solid matter present invariably clogged the opening of the pipette. Another instrument was therefore constructed, consisting of a heavy disc of metal supported in its axis by an elastic steel wire 0·2 m.m. diameter, the torsion of which causes the disc to oscillate when a rotatory motion is imparted to it; the lower end of the steel wire is rigidly attached to a hollow cylinder, open at both ends, which is immersed in the liquid to be heated. The damping effect of the liquids on the motion of the cylinder is a very sensitive measure of their viscosities. The upper surface of the disc is graduated, and a fixed pointer is placed directly above it, so that the degrees of oscillation can be easily observed.

The method of working out the results and plotting curves is very fully discussed, and several examples are given.

The testing of milk with this viscometer requires more care than when perfect solutions or simple liquids are examined. Unless a sample is thoroughly well mixed immediately before an estimation is made the result will not be trustworthy, on account of the cream separating and rising to the surface.

Several tables of the results of testing the milk of different cows are given, and it is found from them that a high coefficient for the fat and a low one for the serum is the most favourable for the economical production of butter. The influence of the viscosity of the milk serum in diminishing the efficiency of the churn has been confirmed by experiments in which viscous substances, such as gum, were added to the milk. A familiar illustration of the influence of viscosity in retarding the action of the churn is furnished by the ordinary method of preparing whipped cream, in which the formation of butter is prevented by adding a little gelatin to the cream.

The second part of this Report treats of the analysis of butters. Several samples of butter, from the Chicago Live Stock Show in 1885, were furnished for examination. The first test was for adulterations by several methods, the chief dependence being placed on Reichert's method of determining the volatile fatty acids. Microscopical examination was also made with a view to testing the value of Dr. Taylor's method, about which there was much difference of opinion. The results, however, were perfectly unsatisfactory. The crystals from all the butters, adulterated as well as genuine, giving a well-defined "St. Andrew's Cross" with polarised light.

Tables of analyses and other data then follow, and the methods of analysis employed are fully described.

In conclusion, we find the daily record of sunshine commenced in May, 1885, but, as these records extend only over two years, they do not yet give sufficient data from which any inference may be drawn.

Cantor Lectures.—The concluding course of Cantor Lectures at the Society of Arts will be on the "Chemistry of Substances taking part in Putrefaction and Antisepsis," by Mr. J. M. Thomson, on May 2, 9, 16, and 23. These lectures are intended to give a general account of the changes occurring during putrefaction, and will deal especially with the properties of the substances resulting from these changes. Special attention will be paid to the chemistry of the common substances employed as antiseptics.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 14, April 4, 1887.

Law of the Distribution of Rays and Bands Common to Several Band-spectra. Analogy with the Law of the Succession of Sounds of a Solid Body.—M. Deslandres.—This paper will be inserted at length.

Determination of Vanadic Acid.—A. Ditte.—This paper also will be inserted in full.

Chemical Function of Manganese and of some other Bodies in Steels.—O. Osmond.—During cooling manganese retards the molecular change of the iron, keeping the carbon in the dissolved state, and the iron in the condition $\beta$ so much the longer as it is present in larger proportion. This action is strictly comparable to that produced upon a non-manganiferous steel containing the same amount of carbon by a more rapid cooling. In a word, it is equivalent to a more or less hard temper. Tungsten possesses the same properties in a more marked degree. Chrome does not appear to act upon the transformation of iron. Silicon is rarely met with in steels, unless accompanied by a greater quantity of manganese. Carbon remains the only steel generating body in the classical sense of the word; the other bodies introduced are merely modifiers.

Certain Ammoniacal Combinations of Cadmium Sulphate and Nitrate.—G. André.—The author gives the details of the preparation of these compounds, and indicates their analogies with the corresponding zinc and copper salts.

Detection and Determination of Vanadium in Rocks and Ores.—L. L'Hote.—(See p. 191).

A New Class of Ferro- and Ferri-cyanides.—J. A. Müller.—The new potassium ferrocyanide crystallises either in very thin scales or in rectangular tablets; 100 parts of water at 18 dissolve 148 parts of the crystalline salt. The solution is neutral to litmus and phenolphthalein, and presents the following reactions with solutions of metallic salts:—With cadmium chloride a milky white precipitate soluble in hydrochloric acid; with cobalt nitrate a peach-coloured precipitate which turns blue on heating and resumes its original colour on cooling; insoluble in hydrochloric acid; copper sulphate an apple-green precipitate; ammoniacal ferrous sulphate a white precipitate, turning blue on the addition of nitric acid; manganese chloride, a bulky white precipitate soluble in hydrochloric acid; ferric chloride a violet colour, and after a day or two a precipitate of the same colour; ammonium molybdate (dissolved in nitric acid), a canary yellow precipitate; gold chloride, a red-brown colour; uranium nitrate, a yellow precipitate verging on orange, insoluble in acetic acid, but soluble in ammonium acetate. The composition of this new ferrocyanide answers to the formula $FeK_3C_6N_5O+3\frac{1}{2}H_2O$, and may be interpreted by admitting the existence of a trivalent radicle, carbonyl ferrocyanogen. Chlorine converts this compound into a new ferricyanide, which gives with ferrous sulphate a blue precipitate, inclining to a violet.

Preparation of Propylamines and Isoamylamines.—H. Malbot.—This paper relates to the propylamines derived from normal propylic alcohol and to the isoamylamines derived from the amylic alchohol of fermentation. These alcohols, duly purified, were converted into hydrochloric ethers, which were then brought to a state of perfect purity. The ethers were then mixed with equal mols. of aqueous ammonia, and heated in closed vessels to 140° to 165° for twelve or twenty-four hours. The tubes were then found to contain two layers, the upper consisting of the secondary and tertiary amines.

On Terpinol.—G. Bouchardat and R. Voiry.—The authors conclude that the substance known as terpinol is a mixture. They have separated from it a compound which they name terpol, which forms five-sixths of the whole, and which is either identical or isomorphous with caoutchine monohydrate. The second product requires further examination.

The Octylic Ethers of the Mono-, Di-, and Trichloracetic Acids.—G. Gehring.—This paper does not admit of useful abridgment.

Detection of Sugar Glucose and Dextrine, added to Wines.—Tony Garcin.—The author determines the total reductive matter with the cuprotartaric liquid and determines the polarimetric deviation. If the proportion of reductive matter is 2 grms. or below, the wine is said to contain a foreign dextro-rotatory matter if its polarimetric deviation exceeds +13.

*Bulletin de la Société Chimique de Paris.* Vol. xlvii., No. 4, February 20, 1887.

Adulteration of Filter-Paper.—L. Padé.—The author has examined ordinary white filter-paper, and finds it to contain 10·4 per cent of total ash. Of this the proportion of calcium sulphate in two samples was found to be respectively 7·6 and 7·4 per cent. The author points out the serious errors and complications which such an impurity may occasion.

*Moniteur Scientifique, Quesneville.* Series 4, Vol. i., March, 1887.

German Chemical Patents.—Preparation of Salols.—Hofmann and Schotensack.—C, No. 2052.

Preparation of Turpentines from the Resins of the Conifers.—Dr. Eugen Schaal.—S, No. 3991.

Preparation of the Ethers of the Fatty Acids.—W. Kirchmann.—K, No. 4729.

Preparation of Derivatives of Phenyl-methyl-oxyquinizine by the Reaction of Hydrazobenzol upon Ethyl-acetone-dicarbonic Ether.—No inventor's name.—G, No. 3697.

Preparation of the Ethylic Ether of a New Acid obtained with Ethylidendiamine and Acetylacetic Acid.—No inventor's name.—G, No. 3734.

Preparation of Oxyquinoleincarbonic Acids.—Dr. F. von Heyden.—H, No. 6336.

Improvement in the Preparation of Blue Sulphuretted Colouring-Matters.—Meister, Lucius, and Brüning.—F, No. 2855.

Preparation of Azo-colours by Means of a New Naphthol-disulphonic Acid.—Drs. O. Gurke and Ch. Rudolph.—G, No. 3636.

Preparation of Azo-colours by Means of the Diazo-Compounds of Diamido-diphenyl-acetone.—Dr. H. Wichelhaus.—W, No. 4260.

Yellow, Red, and Violet Colours prepared with the Tetrazo-derivative of α-Naphthylene-diamine.—No name.—B, No. 7157.

Process for Separating Crude Xylidine from its Isomers employed in Colour-making.—Dr. L. Limpach.—L, No. 3914.

Simplification of the Molybdic Method for the Determination of Phosphoric Acid.—A. von Reis.—Already noticed.

On Cyclamose.—G. Michaud.—From the Chemical News.

Analysis of Commercial Samples of Iodine.—G. Weiss.—From the Chemical News.

Commercial Analyses: Ferric Oxide and Alumina.—From the Chemical News.

Researches on Certain New Azo-Compounds.—Dr. Eugene Mentha.—The author has effected the synthesis of some novel azo-compounds, and especially of a monocarboxylated acid.

Disinfection by Heat.—From *Nature*.

A New Chemical Element.—A notice of germanium. Dr. Quesneville prefers for it Mendeleeff's name ekasilicium, and fears that the name germanium may be mistaken for geranium!

Academy of Medicine.—January 25, 1887.—A discussion—final it is to be hoped—on the use of salicylic acid for the preservation of foods and beverages. Its use was condemned by a very large majority.

Report presented by M. de Luynes on the Utilisation of Naphthaline in the Manufacture of Colouring Matters.—From the *Bulletin de la Société d'Encouragement*.

Chloride of Sulphur and its Use in the Vulcanisation of Caoutchouc.—Ch. A. Fawsett.—From the *Journal of the Society of Chemical Industry*.

New Process for the Production of the Alkaline Metals.—H. Y. Castner.—From the Chemical News.

Combustion of Glycerin by Chromic Acid.—MM. Cross and Bevan.

On the Same Subject.—Dr. Burghardt.—Both these papers are from the Chemical News.

Chemical Constitution of the Fruits of Daphnadium Cubeba.—J. O. Braithwaite and E. H. Farr.—From the *Pharmaceutical Journal*.

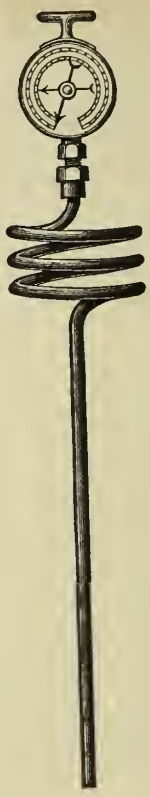
## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Watermark in Paper.—Will any correspondent please inform us as to the best method of putting in a water-mark or imitation water-mark into paper after manufacturing?—Midland, Wolverhampton.

## MEETINGS FOR THE WEEK.

Monday, May 2nd.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "The Chemistry of Substances taking part in Putrefaction and Antisepsis," by J. M. Thomson, F.C.S.
—— Society of Chemical Industry, 8. "Recent Bacteriological Research in connection with Water Supply," by Dr. P. F. Frankland. "The Action of Zinc Chloride on Castor Oil," by Dr. C. R. A. Wright. "Pictet's Wood Pulp System," by Messrs. Cross and Bevan. "The Estimation of Moisture in Superphosphates and similar Fertilisers," by John Ruffle.
—— Royal Institution, 1.30. Annual Meeting.
Tuesday, 3rd.—Institution of Civil Engineers, 8.
—— Pathological, 8.30.
—— Royal Institution, 3. "Electricity," by Prof. W. E. Ayrton, F.R.S.
Wednesday, 4th.—Society of Arts, 8. "Agricultural Education," by J. C. Morton.
Thursday, 5th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "The Chemistry of the Organic World," by Prof Dewar, F.R.S.
—— Chemical, 8. "A Contribution to the Study of Well Waters," by R. Warington. "The Influence of Temperature on the Heat of Dissolution of Salt Solutions," by Prof. Tilden, F.R.S. "The Distribution of Lead in the Brains of Two Lead Factory Operatives Dying Suddenly," by A. Wynter Blyth. "Crystals in Basic Converter Slag," by J. E. Stead and C. H. Ridsdale.
Friday, 6th.—Royal Institution, 9. "The Element of Truth in Popular Beliefs," by Dr. T. L. Brunton, F.R.S.
—— Geologists' Association 8.
Saturday, 7th.—Royal Institution, 3. "Recent Researches on Sponges," by R. Von Lendenfeld, Ph.D.

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THE CHEMICAL NEWS.

Vol. LV. No. 1432

## ON PERBROMIC ACID.

By R. W. EMERSON MACIVOR, F.I.C., F.C.S., &c.,
Formerl Demonstrator of Chemistry, Anderson's College, Glasgow.

In 1863 Kammerer (*Journ. Pr. Chem.*, xc., 190; *Bull. Soc. Chim.*, 1863, i., 129) announced that he had formed perbromic acid by the action of bromine on hydrated perchloric acid, and that from the acid so prepared had made the perbromates of potassium, barium, and silver. In 1874 M. M. P. Muir (*Chem. Soc. Journ.*, 1874) stated that he had succeeded in obtaining perchloric acid by Kammerer's method, and made brief reference to some perbromates which he had prepared from the acid. In 1876 (Chemical News, vol. xxxiii., p. 35) I proved that perbromic acid could not be formed in the manner described by Kammerer and Muir, and that therefore the salts which these chemists had described as perbromates were in reality only perchlorates.. Later in the same year Muir (*Journ. Chem. Soc.*, 1876) contradicted the assertions made in his first paper, and confirmed my results.

Since the publication of my note in 1876 I have at different times, and in different ways, tried to obtain perbromic acid from its chlorine analogue by the action of bromine, but without the least success. Bromine is without action on hydrated perchloric acid, anhydrous perchloric acid, and perbromate of silver, even when the substances are heated together in closed tubes.

## TESTING AND REPORTING ON LUBRICATING OILS.

By THOMAS T. P. BRUCE WARREN.

I am not aware that any one interested in lubricating oils pays much attention to professional reports. I am not myself surprised at this, because of the absence of data which will enable a user of these oils to know the relative merit of an oil in overcoming the friction arising from the movements of a shafting, which after all is the main point of interest to a user of lubricating oils.

Reduction of friction means a saving of coal and diminished wear and tear. From these considerations it follows that economy, as regards price per gallon, is a most unreliable line to follow. A manufacturer is mainly interested in reduced friction, and this friction is so easily compared that it becomes more surprising to meet with its omission so frequently in reports.

In comparing samples of machine oil, the very first test which I apply is to obtain a coefficient for friction. When the bearing has cooled, its condition is examined. It is quite possible that an oil may have so high a viscosity that it will not freely lubricate, and yet our professional reports attach great importance to this. If an oil is too thin, or becomes so by heat due to friction, it will run off a bearing, and so run to waste.

Again, an oil suited for a certain class of machinery may be unfitted for another. In a general factory the main point is to use, for any special machinery, that oil which experience alone can settle as being most beneficial, and to use a general machine oil which will suit the greatest number of bearings.

Defective bearings are sometimes met which will generate heat with one oil and not with another. I am not alluding here to bearings which are downright bad, but to such cases where a bearing is unaccountably critical in spite of engineering workmanship. Such a bearing as this will soon settle the special merits of a lubricator, for a machine oil which will work well on such a bearing will as a rule work well on any other.

An oil which will solidify or thicken at about 40° F., so as not to flow freely, may cause much mischief. A good lubricating oil for general use should be but slightly altered in viscosity between the temperatures of 40° F. and 70° F. Before petroleum lubricating oils came into use, lard oil was used for lubricating cylinders of engines,—the diminished viscosity due to high temperatures was not considered at all as productive of mischief.

Thickened engine oils are now commonly met with which do not flow freely even at 70° F. Such oils are generally produced by adding the tarry residuums obtained from vegetable oils with petroleum of high density, although petroleum oils of high viscosity are well known.

Petroleum oils do not act on brass or the alloys usually employed for bearings; the addition of thickened or slightly oxidised oil, so as to make a more viscid compound, is easily detected by placing a small quantity of the oil in a polished brass cup. If petroleum be not mixed with oil so thickened, its action on metals is only slight after some time; the unoxidised oils are decidedly free from acid, but as they become thickened by exposure their acid reaction is more strongly marked.

A drying oil, or an oil that thickens on exposure, is not regarded favourably as a lubricator, and I think this a matter which deserves more attention than is at present given to it. If such an oil were used by itself it would clog up; the addition of petroleum prevents this clogging by simply acting as a solvent of the oxidised oil; still after some long use such an oil will give trouble.

An engineer will always give preference to an oil free from this tendency to clog. Whenever a drying oil has been added to thicken a machine oil, its presence can always be detected by chloride of sulphur, as referred to in a previous communication.

Petroleum oils, if too thin, should be mixed with animal or fish oils. Purified rosin oil is largely used for lubricating, and, although manufacturers of machine oils condemn its use, I certainly am at a loss to understand upon what ground their objection is based. If a lubricating oil gives any sign of *gumming* up, when a bearing cools, resins, or similar body-giving substances, can be easily detected. Rosin oil does not produce this clogging if properly distilled.

The thickened oils which are used in compounding machine oils are rape oil, cotton-seed oil, and seed oils generally. A few years ago an oil was met with in commerce as "Seed oil." It is probably obtained from "Niger seed," and other unenumerated oil seeds which give the same reaction with chloride of sulphur, and consequently belong to the class of drying oils.

In a future communication I propose to give the analytical details for finding out the composition of a machine oil, and also the mechanical methods for determining the suitability of an oil for machinery.

## DETERMINATION OF VANADIC ACID.

By M. A. DITTE.

The process formerly indicated by Berzelius, the principle of which is the insolubility of ammonium vanadate in ammonium chloride, enables us to determine vanadium in the state of vanadic acid in an exact and relatively simple manner, but on condition of taking certain precautions which are indispensable if we wish to escape error.

Ammonium vanadate is at common temperatures insoluble in a saturated solution of ammonium chloride; if, therefore, we add ammonium chloride to the solution of

an alkaline vanadate, so as to saturate it, all the vanadic acid is precipitated in the form of a white crystalline powder, which is easily collected, and which is washed with a saturated solution of ammonium chloride; but when the washing has removed all foreign matter it is necessary to eliminate the sal-ammoniac in its turn, for if it remains mixed with the ammonium vanadate, or if the filter is still impregnated with it, it is volatilised on igniting the precipitate, reducing the vanadic acid and forming volatile compounds. We then see appear along the edges of the platinum capsule a blue colouration of the flame,—a certain sign that vanadium is being volatilised, and that the determination is inaccurate. The quantity of metal carried off may be considerable if the sal-ammoniac was mixed with the vanadate in a noteworthy proportion; but even if little of it remains it is plain that the same reaction is produced, and gives rise to losses of vanadic acid impossible to estimate.

It is therefore necessary to remove the ammonium chloride entirely, and this can be done by making use of alcohol; but this reagent, if poured upon a filter impregnated with a saturated solution of ammonium chloride, precipitates this latter upon the surface of the filter and even in its thickness, and this salt, sparingly soluble in alcohol, becomes difficult to remove. To use a mixture of water and alcohol is unsafe, for such a mixture—containing even 4 parts of alcohol to 1 part of water—dissolves a little of the vanadate unless it has been previously saturated with sal-ammoniac, which it is then incapable of dissolving. These inconveniences may be avoided in the following manner:—

1. Suppose the vanadic acid existing in solution as a pure alkaline salt. It must first be ascertained that the liquid is neutral or alkaline, for in an acid solution the ammonium vanadate is not completely precipitated. As every acid vanadate is more or less coloured, ammonia is added, and the liquid is heated until it is quite colourless. This decolouration would take place in the cold, but may take several hours. As soon as the temperature of the liquid has fallen to 30° or 40° we throw into it powdered ammonium chloride, little by little, and stir so as approximately to saturate it with this salt., and add to the solution 4 or 5 vols. of alcohol. It is then let stand for some hours, the ammonium chloride being sparingly soluble in this mixture. We have thus a saturated liquid in which the ammonium vanadate is insoluble. If the temperature of the aqueous solution did not exceed 40° when it was saturated with the chloride, the addition of alcohol precipitates only little of this salt, and, as it is very finely divided, washings with alcohol readily dissolve it. After standing for some hours the liquid is filtered, and the precipitate collected upon a filter is washed with alcohol, which does not dissolve the ammonium vanadate in an appreciable proportion. In agitating the aqueous solution with sal-ammoniac for the purpose of saturation it is well to avoid the use of a glass rod, as wherever it touches the glass crystals of vanadate are deposited, which adhere to the sides and are not easily removed with a pencil.

2. When the liquid in which we have to determine vanadic acid contains, in addition to the vanadate, other alkaline salts sparingly soluble in alcohol, they may be deposited along with the ammonium vanadate, and the process requires to be modified. We begin by saturating the liquid with ammonium chloride, of which a small excess is left undissolved; then 4 or 5 vols. of a saturated solution of the same salt are added, and the whole is let settle for some hours. The clear, supernatant liquid, containing the greater part of the foreign salts, is decanted through a filter, and it is replaced by fresh solutions of ammonium chloride, always taking care to leave a little of the undissolved salt. After standing five or six hours the decantation is resumed through the same filter, and, according to circumstances, the washing is repeated once or several times. Lastly, the filter is pierced, washed with boiling water to remove any traces of ammonium vanadate which may have been carried over during the decantations. The washing water is received in the glass containing the precipitate of ammonium vanadate which is partially re-dissolved. The new liquid thus obtained is free from foreign salts. It is saturated at 40° with ammonium chloride, and the operation is concluded as already described.

3. The filter containing the ammonium vanadate, well washed with alcohol, is dried in the stove. The deposit is let fall into a platinum capsule, the filter is placed above it, and it is heated gradually to redness. The filter burns, the vanadate is decomposed, the carbon of the filter burns in the air, and, lastly, the mass melts. It is kept for some time in fusion, so as to effect complete oxidation, and the capsule is weighed when cold.

When operating thus upon a few decigrms. of vanadic acid we might fear the formation of small quantities of the compound $VO_4,VO_5$, which is very difficult to oxidise under the circumstances. To avoid this slight cause of error the ignition is effected at dull redness, and, without troubling about burning the carbon of the filter, it, as well as the pulverulent matter arising from the decomposition of the ammonium vanadate, is moistened with a little pure nitric acid, and evaporated to dryness. The oxides of vanadium are converted into vanadic acid. The residue after evaporation is heated to redness, the relics of the filter quickly disappear, the vanadic acid melts, and is weighed when the crucible is cold.

4. If the vanadic acid is not in the state of an alkaline salt it must be converted into such, and the foreign oxides must be removed. The method of this operation varies according to the oxides present, and is often difficult. When the vanadium has been obtained as an alkaline vanadate the determination is effected as explained above. —*Comptes Rendus* (civ., p. 982).

## THE LAW OF THE DISTRIBUTION OF RAYS AND BANDS COMMON TO SEVERAL BAND-SPECTRA.

## ANALOGY WITH THE LAW OF SUCCESSION OF SOUNDS OF A SOLID BODY.

By M. DESLANDRES.

In a former communication the author has indicated a simple law which governs the distribution of the rays of one and the same band (*Comptes Rendus*, vol. ciii., p. 375), and which may thus be summarised:—In general the rays which compose one and the same band may be divided into series of identical rays entangled with each other, and such that in each series the intervals from one ray to the next following form approximately an arithmetical progression. Now this simple law of distribution is applicable also to the bands of one and the same band spectrum, and this new extension of the law forms the subject of the present paper.

The author represents a band by the original ray of one of its component arithmetical series, the original ray being the one placed at the extremity of the series on the side of the smallest intervals, and he has studied the distribution of these original rays. Now, when these rays are expressed in numbers of vibrations, he has again found, in a certain number of spectra, the simple law already indicated for the rays of one and the same band. The original rays may be divided into series, which have also this common property, that the intervals of one and the same series form approximately an arithmetical progression.

The first spectrum in which this law of distribution has been verified is the second group of the bands of nitrogen (from $\lambda$ 500 to $\lambda$ 280), which is remarkable for its great extent and its regularity; it presents at least fifty bands, and each band is formed by superposition of three equal and equidistant arithmetical series. In what follows the

author considers only the original ray of the arithmetical series of the middle.

The description of the indices peculiar to this spectrum, which have led to its discovery, would present a certain interest, but it would take up too much space. The author's paper was accompanied by a diagram showing the five arithmetical series, which are equal in this spectrum, and which comprise all the original rays, whilst a table shows the agreement between the numbers as observed and as calculated.

In a former memoir he represented the rays of one and the same band by the formula $Am^2 + \alpha$, $m$ being an entire number, which varies from 1 in 1, 2 in 2, 3 in 3, &c. In like manner the original rays of each series of bands will be given by the formula $Bn^2+C$, and the totality of the rays of a series by $Am^2+Bn^2+C$. The fourth series of the second group of nitrogen is thus represented by the formula $0{\cdot}145735 \times n^2 - 152{\cdot}533$.

The author has also verified the law in the following spectra: the third positive group of nitrogen (from $\lambda$ 300 to $\lambda$ 200), the original rays of which form four series; the group of the negative pole of nitrogen, with five series, the coefficient B of the two foregoing spectra being nearly equal to the coefficient B of the second group of nitrogen; the first positive group of nitrogen (from $\lambda$ 700 to $\lambda$ 500) with at least 3 series, which Dr. Hasselberg's accurate measurements render it possible to find; the spectrum ascribed to the hydrocarbons and that of carbon monoxide; lastly, the primary spectrum of iodine, which M. Thalen has decomposed into seven similar series. Now, if we express the bands in numbers of vibrations these series become progressions, and it is thus that the 36 bands of the first series are represented by the formula—

$$N = 198{\cdot}964 - 0{\cdot}0102985 \times n^2,$$

$n$ varying from 16 to 51. The agreement with the numbers observed is sufficiently distinct, notwithstanding the smallness of the ratio in relation to the possible error in measurement.

This law, if we consider the number and the origin of the spectra cited, appears general, and it points to a common structure in spectra at first sight unlike, as the spectra of iodine and of the hydrocarbons. Further, if we prolong from the side of the smallest intervals the progressions of these spectra, which present only in general large intervals, we arrive at an entanglement of bands, which recalls the confused aspect of spectra more complex in appearance, such as those of bromine and of hyponitric acid. It is therefore permissible to hope that these spectra also may be referred to this general law.

But the author has carried this study still further for certain spectra, and in particular for the second group of nitrogen. He has prolonged from the side of the smallest intervals the five progressions which comprise all the bands, and he has examined if the originals of these new progressions were also connected by the same simple law. These originals are given by the constants of the formulæ $Am^2 + Bn^2 + C$, and are equal to $-134{\cdot}151$, $-152{\cdot}533$, $-171{\cdot}268$, $-190{\cdot}687$, $-210{\cdot}623$. Now the squares of these constants have intervals which form an arithmetical progression. We therefore substitute C by $\sqrt{Cp^2+y}$, $p$ being a whole number.

On the other hand, the coefficient A has not the same value for all the bands of the spectrum. It appears to be a simple function of the parameters $n^2$ and $p^2$, which define the original ray of the band, but the study of this function is not completed, and in order to be executed with the accuracy desirable it requires a dispersion higher than that at the author's disposal. In any manner the spectrum considered may be represented by three almost identical formulæ, of the form $f(n^2, p^2) \times m^2 + Bn^2 - \sqrt{Cp^2+y}$.

These three formulæ correspond to the three identical and closely approximating arithmetical series (distant at most by $0^{N}{\cdot}100$) which compose each band of the group. The spectrum of the negative pole, the bands of which present a single series, will be represented by a single formula.

The above formula indicates a very distinct analogy between the distribution of the spectral rays and the succession of sounds of a solid body.—*Comptes Rendus*, civ., p. 972.

## THE HARDNESS OF METALS.*

By THOMAS TURNER, Assoc. R.S.M., F.C.S.,
Lecturer on Metallurgy, Mason College, Birmingham.

(Continued from p. 196.)

During last summer I had occasion to perform a number of tests of the hardness of cast-iron, at the Rosebank Foundry, Edinburgh. In this case a diamond was employed as before, but a balanced and graduated metal beam was used, the pressure being obtained by means of a sliding weight of about 80 grms. These results are given in Table C, and will be again mentioned. They agree fairly well with my other observations, though another diamond was employed with the modified apparatus.

My present arrangement is as follows (Fig. 3):—

It consists of a balanced and graduated beam of gun-metal, A, working on steel knife-edges, B, and counterpoised by means of the large sliding weight, F, the final adjustment being obtained by the screw, G. When balanced it is sensitive to 0·01 grm. at E, though such delicacy is probably not required. The knife-edges rest upon planes in the support, C, which is capable of rotating on a steel pivot connected with the rod, D. The diamond is mounted in a brass tube, having a milled head, and which is fixed by means of a screw at E. The specimen to be tested, which often takes the form shown, J, is supported by a wooden block, K. The weight, H, is arranged so that each division on the graduated scale shall correspond to a pressure of a grm. at the diamond point. Thus, at division 12, we have a pressure of 12 grms. on the diamond. Three extra weights, I, are used when necessary; they are each of the same weight as H. Hence, with one weight, scale division 10 corresponds to 10 grms. on the diamond, with two weights 10 corresponds to 20 grms., with three weights to 30 grms., and with four weights to 40 grms.; the other scale divisions being read in an exactly similar manner. It will be noticed that the specimen is stationary, while the diamond is moved, thus differing from the sclerometer as applied to minerals; the method of supporting the beam and of applying the weight is also different. In ordinary experiments, where considerable weights are applied, the diamond may be moved by the finger, and, as the apparatus is very steady in its action, with a little care this gives very concordant results. For more delicate observations, with smaller weights, the diamond may be drawn by means of a horizontal string running over a small pulley. The surface used is prepared roughly in the ordinary way by chipping, filing, &c., and then with a smooth file; it is finished with emery paper, using at least the finest variety, or flour, emery, and oil, according to the material. It should be finished all one way, so as not to leave small irregular scratches, and should be as smooth and bright as possible. As a rule an experienced workman should not take more than half-an-hour in preparing such a specimen, though occasionally a hard material will take longer. If the surface tested be rough the results are erroneous, being generally higher than with a good surface. It can, however, be told at once on inspection whether a surface is suitable for the purpose. If any doubt should exist, another smooth face must be prepared, and the experiment continued until uniform results are obtained.

Reference has already been made to the difficulty of reading the scratch, or, in other words, of detecting when

* Read before the Birmingham Philosophical Society, Dec. 9, 1886

abrasion begins. If the scratch is always read in the same way, uniform results can be obtained, but the actual value will depend upon the standard scratch used in the experiments. It is doubtless from this cause that my own values are higher than those of Franz, as will be shown later, though each set of experiments is in itself uniform.

In viewing a scratch on a smooth metallic surface there are two principal appearances observed. When viewed at certain angles, so that the metal is dark, the scratch is seen as a bright line; while if the metal is seen in another direction the scratch appears as a *dark* line on a bright surface. A smaller weight is required to produce a visible scratch if it be viewed as a bright line than if it appear a dark line on a bright surface. In my experiments the scratch was always viewed as a *dark* line, for the following reasons:—

1. With a little experience, uniform results can be obtained in different observations on the same specimen.
2. The scratch produced being somewhat deeper when read by this method, a greater range is obtained with the instrument.
3. Because, as will be afterwards shown, this depth of scratch probably corresponds as nearly as possible with the beginning of abrasion.

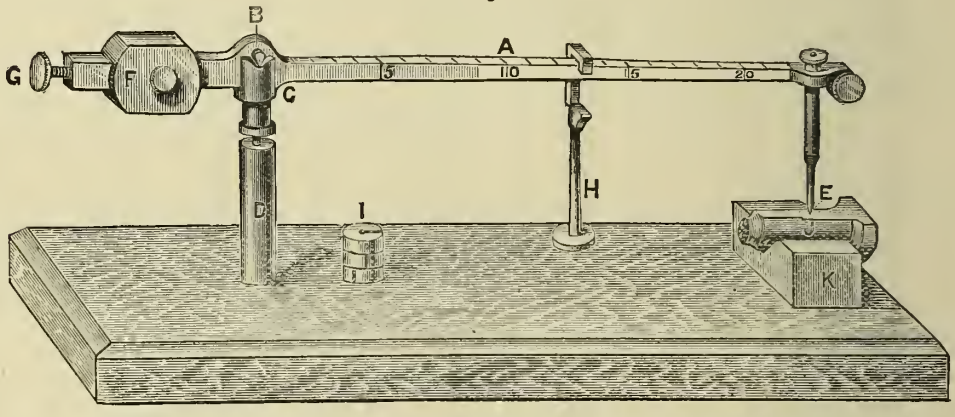
Attempts were made to read the scratch by means of a lens or a microscope, but without much success.

When magnified, the scratches produced by gradually increasing weights appear to change by almost imperceptible degrees, and no definite point can be fixed upon as that at which the action commences. But on comparing a deep scratch with a very faint one a marked difference can be seen. In the case of a light scratch the surface appears to be merely smoothed over by the passage of the diamond, while with a deeper scratch the material is torn up, and a distinct ridge produced. In my method of observing the scratch I have endeavoured to take that point at which this tearing up of the surface, or abrasion, begins. Even when viewed under the microscope this point is not definite, and hence the method I employed must be regarded merely as an arbitrary one, intended to approach as nearly as possible to the theoretical conception. In these experiments three different diamonds have been employed, and very concordant results obtained in each case, care being taken always to work as nearly as possible in the same manner. The diamond is octahedral, and set so that the point of the crystal is used to produce the scratch. After considerable wear I have not detected any alteration in the weight required to mark a given specimen. The excellent wear of the diamond is probably due to the fact that the heaviest weight used is only 92 grms., or about three ounces. But though the diamond thus appears to have little effect on the results, the influence of a rough surface, a bad light, or a different method of observation, is very considerable. The character of the surface has already been sufficiently explained. A bright diffused light is best, and the specimen should be placed near to a window, and in such a position that the reflection from bright objects in the room, white walls, &c., should interfere as little as possible. From this cause it will be found extremely difficult to obtain accurate results in some positions.

As it has been suggested that this apparatus might be very useful for practical purposes, and several practical men have already expressed their intention of adopting it, I shall venture to give a detailed description of the method of observation.*

The surface of the metal having been properly prepared, and a suitable position as regards light having been chosen, the specimen is fixed horizontally under the point of the diamond. By means of the movable weight (F) and adjusting screw (G) the diamond is now carefully balanced just above the smooth surface. The four weights are then placed on the beam in such a position that a definite scratch is produced on drawing the diamond over the metal; the point being drawn once forward and once backwards over the same line. A definite scratch, necessary to guide the eye, having been thus produced, the weights are placed on a lower scale division and another scratch made parallel to the first; this being repeated as often as necessary, the weight meanwhile being gradually reduced. In the case of a mild steel requiring a weight of 21 grms. the weights might at first be placed, say, at 15, then at 10, afterwards at 9, 8, 7, 6, 5, and 4 in

Fig. 3.




A. Beam.
B. Knife-edge.
C. Rotating Support.
D. Steel Rod and Pivot.
E. Diamond.
F. Sliding Weight.
G. Adjusting Screw.
H. Sliding Weight.
I. Extra Weights.
J. Test Piece.
K. Wooden Support.

* Arrangements are being made with a Birmingham firm for the supply of this form of apparatus to manufacturers and others to whom it might be useful. I shall be glad to examine each sclerometer before it is sent out for those who may desire it.

succession, a number of parallel lines being made which viewed as bright lines on a dark surface appear as in A, gradually becoming less distinct, but all clearly visible. But on viewing the same lines at the proper angle, as dark lines on a bright surface, they would appear as in B, No. 6 being very faint, while No. 5 is invisible, or only seen with the greatest difficulty, and No. 4 is visible.

The result is, therefore, as follows:—

| Scale Division. | Weight in Grms. | Result. |
|---|---|---|
| 15 | 15×4=60 | Plainly visible. |
| 10 | 40 | ,, |
| 9 | 36 | Visible. |
| 8 | 32 | ,, |
| 7 | 28 | ,, |
| 6 | 24 | Faintly visible. |
| 5 | 20 | Value taken. |
| 4 | 16 | Invisible. |

By means of the four weights, therefore, it has been shown that the hardness is somewhere between 16 and 24. A similar series of operations is now gone through with three weights on the beam, when probably a value of 7, equal to a weight of 21 grms., would be obtained.

On using two weights, probably a value of 11 would be obtained, corresponding to a weight of 22 grms. It will be pretty certain from these experiments, if carefully performed, that the true value must lie about 20—22 grms. The number is now determined by means of the single weight. For this purpose a distinct line is made, so as to guide the eye, and then a series of parallel lines are made, beginning with division 24 perhaps, and ending with about 18. The specimen is then carefully examined and the proper line chosen; the experiment being repeated until a satisfactory result is obtained. With practice, uniform values are obtained for the same specimen, and the error should not exceed $\pm$ 5 per cent. In cases of doubt, it is very easy to refer to a standard specimen, and the whole operation generally occupies about a quarter of an hour. A novice can at once distinguish between specimens that differ much in hardness, as for instance in the examples given in Tables A and B; but experience is required before different specimens of pretty uniform hardness, such as mild steel, can be distinguished.

(To be continued).

## THE ANALYSIS OF SUGAR-CANE AND BEET JUICES, WITH A TABLE FOR THE CALCULATION OF ANALYSES.

By C. A. CRAMPTON.

In the routine work of cane- and beet-sugar houses, the greater part consists in the analysis of large numbers of samples of juice. A method of manipulation for these analyses is therefore desirable which will unite a reasonable degree of accuracy with considerable speed. It is from the desire of contributing to this end that this article was written, and not with the intention of presenting anything new in the way of processes. The method and routine of analysis given below has been pursued by myself and others for several years in the work of the U. S. Department of Agriculture, in its experiments on sorghum and sugar-cane, and found very expedient in the brief "sugar season," when the saving of time is so important an object. For very accurate work, of course, it is necessary to weigh out the sample of juice taken for analysis, but for all ordinary purposes the sample may be measured by volume, increasing greatly thereby the rapidity of the operations. By taking the sp. gr. with accurate spindles, having their graduations well spaced, and correcting the valence taken, a very close approximation to the actual weight is obtained; the correction may be applied in two ways:—

1. By dividing the normal weight for the polariscope, or a multiple of it, by the sp. gr. of the juice, to find the number of c.c. of the liquid exactly corresponding to this weight, and then measuring out this quantity from a burette into a 100 c.c. flask, adding subacetate of lead solution, making up the volume to 100 c.c., filtering, and polarising. The reading of the polariscope gives directly the per cent of sugar in the juice, only multiplied by the number of times the normal weight was taken.

2. By measuring out a certain volume of the juice, adding lead solution, making up to another definite volume, and polarising and applying the correction for sp. gr. to the reading obtained.

I prefer the latter method as more expeditious and convenient, for in the other the sp. gr. must be determined and a calculation made, before the sample for polarisation can be taken; while in the second method the sp. gr. may be taken at any time through the day, and the calculation of the results postponed indefinitely.

The custom among sugar chemists in the best houses in France and Germany is to measure 100 c.c. of juice in a flask graduated to 100 and 110 c.c., add 10 c.c. of a dilute solution of subacetate of lead, filter, and polarise; the increase in volume being corrected, either by reducing in a 220 m.m. tube, or by adding one-tenth to the reading. I have found it more advantageous however, to take 50 c.c. of the juice, add lead, and make the volume up to 100; this gives a much more satisfactory liquid for polarisation, especially with impure juices, and the filtration is greatly facilitated. The only object attained by using 100 c.c. is the increase of the reading, and consequent lessening of errors of observation; this is of but little importance, however, as 50 c c. is two or three times the normal quantity for most instruments. Even this objection may be done away with by using a double length (400 m.m.) tube, providing the instrument used will admit of the long tube, and this is entirely practicable as far as the lucidity of the solution is concerned, for I have never failed to get clean bright solutions by proceeding in the manner I have indicated, except in cases where juices had been allowed to stand, and mucous fermentation had set in.

The detailed procedure is as follows:—

50 c.c. of the juice is measured out by means of an accurately calibrated pipette, and run into a 100 c.c. flask; to it is added from 1 to 4 c.c. of a strong solution of subacetate of lead,* the whole made up to the mark with water, filtered, and polarised.

The same solution is then used for the determination of the reducing sugars by Fehling's solution—the excess of lead being precipitated by sulphate of soda. As the reduction of copper suboxide by sugars has been shown to be affected by the amount of dilution in which the action takes place, it is desirable to have, as nearly as possible, a constant amount of dilution, and the most favourable dilution is such, that from 10 to 20 c.c. of the solution will be required to reduce the copper from 10 c.c. of Fehling's solution; so, for juice presumed to contain from 1 to 2 per cent of reducing sugars, 50 c.c. of the solution which has been polarised, made up to 100 c.c., will furnish the proper dilution; for those containing from 2 to 3 per cent, 50 c.c. to 150 c.c., and so on. In the case of juices containing less than 1 per cent of reducing sugars, the excess of lead may be removed by adding the sodic sulphate† before the lead precipitate is filtered off, when the same solution can be used for polarisation and for the reducing sugar determination. The copper solution used is Violetti's modification, and the operation is performed in large test-tubes, 9 to 10 inches long, and of about 1 to 1½ in. calibre, and the end reaction is obtained with ferro-

* Prepared by rubbing up in a mortar 1 kilo. of subacetate of lead with ½ kilo. of litharge, and boiling with ½ litre of water.

† For very exact work it is better to take a separate sample of the juice for the copper test, and to dispense with lead altogether if the purity of the juice admits, for the presence of lead produces an error and even when precipitated by sulphate of soda there is said to be an error, from the slight solubility of the sulphate of lead.

cyanide of potash and acetic acid, the small portion of clear liquid required being filtered out by means of Wiley's tubes, already described.* These tubes are simply glass ubes about 9 to 10 in. long and ¼ in. in calibre; at one extremity a slight rim is made by turning back the edge while hot, and over this is stretched and tied a piece of fine linen cloth. To use the tube, it is inserted into a beaker of water, containing in suspension a quantity of very finely ground asbestos pulp; by suction at the other end of the tube, the linen cap is covered with a film of asbestos, and it is then immediately inserted into the test-tube containing the hot precipitated Fehling's solution; suction is again made on the tube, and the portion of clear liquid obtained is run into the porcelain dish containing the test solution by simply inverting the tube. These tubes may be cleaned and used over and over again by washing off the asbestos film, dissolving out any suboxide of copper which may remain in the cloth by soaking in nitric acid and rinsing in water until they no longer taste acid. One covering of linen suffices for many tests, and when worn out it is easily replaced.

Working in this way a large number of samples can be analysed in a day—25 to 30 being generally a fair day's work for operators on the stations of the Department of Agriculture, both sucrose and glucose being determined, and also the total solids (from the sp. gr.), and this number is much exceeded, in case of stress of work, by allowing the polarisations to stand over until night, using all the daylight for glucose determinations. By having a boy to measure out the samples and prepare them for analysis the amount of work done can be nearly doubled.

It remains to calculate the results obtained, and to facilitate this calculation I have compiled the following table. In it will be found the sp. gr. and degree Brix,† and opposite to him factors for the calculation of sucrose and glucose in juices of the corresponding sp. gr., according to the method of procedure given above. Two factors for sucrose are given, one for instruments using as a normal quantity 26·048 grms., such as the Soleil-Schiebler, and one for those using 16·3 grms., such as the Laurent.‡ These factors are the quotients arising from division of the normal quantities by (50 × sp. gr.), and to use them it is necessary simply to multiply them by the reading of the polariscope, the result giving directly the per cent of sucrose in the juice. The glucose factor is simply the reciprocal of the sp. gr. with the decimal point changed. To use it, it is divided by the number of c.c. of the normal solution (50 c.c. of juice to 100) required to precipitate 10 c.c. of Fehling's solution, which gives the result directly in per cents. If the solution has been diluted twice (50 c.c. to 200) divide the factor by half the number of c.c. required, if one and a half times (50 c.c. to 150) by one and a half times the number of c.c. required, and so on.

TABLE FOR CALCULATION OF ANALYSES OF CANE AND BEET JUICES.

| Specific gravity. | Degree Brix. | Sucrose factor for instruments requiring 26·048 grms. | Sucrose factor for instruments requiring 16·3 grms. | Glucose factor. |
|---|---|---|---|---|
| 1·0197 | 5·0 | 0·5109 | 0·3197 | 9·807 |
| 1·0201 | 5·1 | 0·5107 | 0·3196 | 9·803 |
| 1·0205 | 5·2 | 0·5105 | 0·3195 | 9·799 |
| 1·0209 | 5·3 | 0·5103 | 0·3193 | 9·795 |
| 1·0213 | 5·4 | 0·5101 | 0·3192 | 9·791 |
| 1·0217 | 5·5 | 0·5099 | 0·3191 | 9·788 |
| 1·0221 | 5·6 | 0·5097 | 0·3190 | 9·784 |
| 1·0225 | 5·7 | 0·5095 | 0·3189 | 9·780 |
| 1·0229 | 5·8 | 0·5093 | 0·3187 | 9·776 |
| 1·0233 | 5·9 | 0·5091 | 0·3186 | 9·772 |
| 1·0237 | 6·0 | 0·5089 | 0·3185 | 9·768 |
| 1·0211 | 6·1 | 0·5087 | 0·3184 | 9·765 |
| 1·0245 | 6·2 | 0·5085 | 0·3183 | 9·761 |
| 1·0249 | 6·3 | 0·5083 | 0·3182 | 9·757 |
| 1·0253 | 6·4 | 0·5081 | 0·3181 | 9·753 |
| 1·0257 | 6·5 | 0·5079 | 0·3180 | 9·749 |
| 1·0261 | 6·6 | 0·5077 | 0·3178 | 9·746 |
| 1·0265 | 6·7 | 0·5075 | 0·3177 | 9·742 |
| 1·0269 | 6·8 | 0·5073 | 0·3175 | 9·738 |
| 1·0273 | 6·9 | 0·5071 | 0·3174 | 9·734 |
| 1·0277 | 7·0 | 0·5069 | 0·3173 | 9·730 |
| 1·0281 | 7·1 | 0·5067 | 0·3171 | 9·727 |
| 1·0286 | 7·2 | 0·5065 | 0·3170 | 9·723 |
| 1·0290 | 7·3 | 0·5063 | 0·3169 | 9·719 |
| 1·0294 | 7·4 | 0·5061 | 0·3167 | 9·715 |
| 1·0298 | 7·5 | 0·5059 | 0·3166 | 9·711 |
| 1·0302 | 7·6 | 0·5057 | 0·3164 | 9·707 |
| 1·0306 | 7·7 | 0·5055 | 0·3163 | 9·703 |
| 1·0310 | 7·8 | 0·5053 | 0·3162 | 9·699 |
| 1·0314 | 7·9 | 0·5051 | 0·3160 | 9·696 |
| 1·0318 | 8·0 | 0·5049 | 0·3159 | 9·692 |
| 1·0322 | 8·1 | 0·5047 | 0·3158 | 9·688 |
| 1·0327 | 8·2 | 0·5045 | 0·3157 | 9·684 |
| 1·0231 | 8·3 | 0·5043 | 0·3156 | 9·680 |
| 1·0335 | 8·4 | 0·5041 | 0·3154 | 9·676 |
| 1·0039 | 8·5 | 0·5039 | 0·3153 | 9·672 |
| 1·0343 | 8·6 | 0·5037 | 0·3152 | 9·668 |
| 1·0347 | 8·7 | 0·5035 | 0·3151 | 9·665 |
| 1·0351 | 8·8 | 0·5033 | 0·3150 | 9·661 |
| 1·0355 | 8·9 | 0·5031 | 0·3148 | 9·657 |
| 1·0359 | 9·0 | 0·5029 | 0·3147 | 9·653 |
| 1·0364 | 9·1 | 0·5027 | 0·3146 | 9·649 |
| 1·0368 | 9·2 | 0·5025 | 0·3144 | 9·645 |
| 1·0372 | 9·3 | 0·5023 | 0·3143 | 9·641 |
| 1·0376 | 9·4 | 0·5021 | 0·3142 | 9·638 |
| 1·0380 | 9·5 | 0·5019 | 0·3141 | 9·634 |
| 1·0384 | 9·6 | 0·5017 | 0·3140 | 9·630 |
| 1·0388 | 9·7 | 0·5015 | 0·3138 | 9·626 |
| 1·0393 | 9·8 | 0·5013 | 0·3137 | 9·622 |
| 1·0397 | 9·9 | 0·5011 | 0·3136 | 9·618 |
| 1·0401 | 10·0 | 0·5009 | 0·3134 | 9·614 |
| 1·0405 | 10·1 | 0·5007 | 0·3133 | 9·611 |
| 1·0409 | 10·2 | 0·5005 | 0·3132 | 9·607 |
| 1·0413 | 10·3 | 0·5003 | 0·3131 | 9·603 |
| 1·0418 | 10·4 | 0·5001 | 0·3129 | 9·599 |
| 1·0422 | 10·5 | 0·4999 | 0·3128 | 9·595 |
| 1·0426 | 10·6 | 0·4997 | 0·3127 | 9·591 |
| 1·0430 | 10·7 | 0·4995 | 0·3126 | 9·588 |
| 1·0434 | 10·8 | 0·4993 | 0·3125 | 9·584 |
| 1·0439 | 10·9 | 0·4991 | 0·3123 | 9·580 |
| 1·0443 | 11·0 | 0·4989 | 0·3122 | 9·576 |
| 1·0447 | 11·1 | 0·4987 | 0·3121 | 9·572 |
| 1·0451 | 11·2 | 0·4985 | 0·3119 | 9·568 |
| 1·0455 | 11·3 | 0·4983 | 0·3118 | 9·565 |
| 1·0459 | 11·4 | 0·4981 | 0·3117 | 9·561 |
| 1·0464 | 11·5 | 0·4979 | 0·3115 | 9·557 |
| 1·0468 | 11·6 | 0·4977 | 0·3114 | 9·553 |
| 1·0472 | 11·7 | 0·4975 | 0·3113 | 9·549 |
| 1·0476 | 11·8 | 0·4973 | 0·3112 | 9·545 |
| 1·0481 | 11·9 | 0·4971 | 0·3110 | 9·541 |
| 1·0485 | 12·0 | 0·4969 | 0·3109 | 9·537 |
| 1·0489 | 12·1 | 0·4967 | 0·3108 | 9·534 |
| 1·0493 | 12·2 | 0·4965 | 0·3107 | 9·530 |
| 1·0497 | 12·3 | 0·4963 | 0·3106 | 9·527 |
| 1·0502 | 12·4 | 0·4961 | 0·3104 | 9·523 |
| 1·0506 | 12·5 | 0·4959 | 0·3103 | 9·519 |
| 1·0510 | 12·6 | 0·4957 | 0·3102 | 9·515 |
| 1·0514 | 12·7 | 0·4955 | 0·3101 | 9·511 |
| 1·0519 | 12·8 | 0·4953 | 0·3099 | 9·507 |
| 1·0523 | 12·9 | 0·4951 | 0·3098 | 9·503 |
| 1·0527 | 13·0 | 0·4949 | 0·3097 | 9·499 |
| 1·0531 | 13·1 | 0·4947 | 0·3096 | 9·496 |
| 1·0536 | 13·2 | 0·4945 | 0·3094 | 9·491 |
| 1·0540 | 13·3 | 0·4943 | 0·3093 | 9·488 |

* *Bull. de l'Ass. des Chim. de Sucr. et de Dist.*, ii., 108.

† Taken from the tables of Mategczek, Schiebler, and Stamme, as given by Dr. Tucker in his "Manual of Sugar Analysis."

‡ For the accuracy of this quantity for Laurent's polariscope see *Bull. de l'Assoc. des Chim. de Sucr. et de Dist.*, 1885, Nos. 8 and 9, p. 255, and *Ann. Chem. Jour*, viii., p. 51.

| Specific gravity. | Degree Brix. | Sucrose factor for instruments requiring 26·048 grms. | Sucrose factor for instruments requiring 16·3 grms. | Glucose factor. |
|---|---|---|---|---|
| 1·0544 | 13·4 | 0·4941 | 0·3092 | 9·484 |
| 1·0548 | 13·5 | 0·4939 | 0·3091 | 9·480 |
| 1·0553 | 13·6 | 0·4937 | 0·3090 | 9·476 |
| 1·0557 | 13·7 | 0·4935 | 0·3088 | 9·472 |
| 1·0561 | 13·8 | 0·4933 | 0·3087 | 9·469 |
| 1·0566 | 13·9 | 0·4931 | 0·3085 | 9·464 |
| 1·0570 | 14·0 | 0·4929 | 0·3084 | 9·461 |
| 1·0574 | 14·1 | 0·4927 | 0·3083 | 9·457 |
| 1·0578 | 14·2 | 0·4925 | 0·3082 | 9·453 |
| 1·0583 | 14·3 | 0·4923 | 0·3080 | 9·449 |
| 1·0587 | 14·4 | 0·4921 | 0·3079 | 9·446 |
| 1·0591 | 14·5 | 0·4919 | 0·3078 | 9·442 |
| 1·0596 | 14·6 | 0·4917 | 0·3077 | 9·438 |
| 1·0600 | 14·7 | 0·4915 | 0·3076 | 9·434 |
| 1·0604 | 14·8 | 0·4913 | 0·3074 | 9·430 |
| 1·0609 | 14·9 | 0·4911 | 0·3073 | 9·426 |
| 1·0613 | 15·0 | 0·4909 | 0·3072 | 9·422 |
| 1·0617 | 15·1 | 0·4907 | 0·3071 | 9·419 |
| 1·0621 | 15·2 | 0·4905 | 0·3069 | 9·415 |
| 1·0626 | 15·3 | 0·4903 | 0·3068 | 9·411 |
| 1·0630 | 15·4 | 0·4901 | 0·3067 | 9·407 |
| 1·0634 | 15·5 | 0·4899 | 0·3066 | 9·404 |
| 1·0639 | 15·6 | 0·4897 | 0·3064 | 9·399 |
| 1·0643 | 15·7 | 0·4895 | 0·3063 | 9·396 |
| 1·0647 | 15·8 | 0·4893 | 0·3062 | 9·392 |
| 1·0652 | 15·9 | 0·4891 | 0·3061 | 9·388 |
| 1·0656 | 16·0 | 0·4889 | 0·3059 | 9·385 |
| 1·0660 | 16·1 | 0·4887 | 0·3058 | 9·381 |
| 1·0665 | 16·2 | 0·4885 | 0·3057 | 9·377 |
| 1·0669 | 16·3 | 0·4883 | 0·3056 | 9·373 |
| 1·0674 | 16·4 | 0·4881 | 0·3054 | 9·369 |
| 1·0678 | 16·5 | 0·4879 | 0·3053 | 9·365 |
| 1·0682 | 16 6 | 0·4877 | 0·3052 | 9·362 |
| 1·0687 | 16·7 | 0·4875 | 0·3051 | 9·358 |
| 1·0691 | 16·8 | 0·4873 | 0·3049 | 9·354 |
| 1·0695 | 16·9 | 0·4871 | 0·3048 | 9·350 |
| 1·0700 | 17·0 | 0·4869 | 0·3047 | 9·346 |
| 1·0704 | 17·1 | 0·4867 | 0·3046 | 9·342 |
| 1·0709 | 17·2 | 0·4865 | 0·3044 | 9·338 |
| 1·0713 | 17·3 | 0·4863 | 0·3043 | 9·334 |
| 1·0717 | 17·4 | 0·4861 | 0·3042 | 9·331 |
| 1·0722 | 17·5 | 0·4859 | 0·3041 | 9·327 |
| 1·0726 | 17·6 | 0·4857 | 0·3039 | 9·323 |
| 1·0730 | 17·7 | 0·4855 | 0·3038 | 9·320 |
| 1·0735 | 17·8 | 0·4853 | 0·3037 | 9·315 |
| 1·0739 | 17·9 | 0·4851 | 0·3036 | 9·312 |
| 1·0744 | 18·0 | 0·4849 | 0·3034 | 9·308 |
| 1·0748 | 18·1 | 0·4847 | 0·3033 | 9·304 |
| 1·0753 | 18·2 | 0·4845 | 0·3032 | 9·390 |
| 1·0757 | 18·3 | 0·4843 | 0·3031 | 9·296 |
| 1·0761 | 18·4 | 0·4841 | 0·3029 | 9·293 |
| 1·0766 | 18·5 | 0·4839 | 0·3028 | 9·289 |
| 1·0770 | 18·6 | 0·4837 | 0·3027 | 9·285 |
| 1·0775 | 18·7 | 0·4835 | 0·3026 | 9·281 |
| 1·0779 | 18·8 | 0·4833 | 0·3024 | 9·277 |
| 1·0783 | 18·9 | 0·4831 | 0·3023 | 9·274 |
| 1·0788 | 19·0 | 0·4829 | 0·3022 | 9·270 |
| 1·0792 | 19·1 | 0·4827 | 0·3021 | 9·266 |
| 1·0797 | 19·2 | 0·4825 | 0·3019 | 9·262 |
| 1·0801 | 19·3 | 0·4823 | 0·3018 | 9·258 |
| 1·0806 | 19·4 | 0·4821 | 0·3017 | 9·254 |
| 1·0810 | 19·5 | 0·4819 | 0·3016 | 9·251 |
| 1·0815 | 19·6 | 0·4817 | 0·3014 | 9·246 |
| 1·0819 | 19·7 | 0·4815 | 0·3013 | 9·243 |
| 1·0824 | 19·8 | 0·4813 | 0·3012 | 9·239 |
| 1·0828 | 19·9 | 0·4811 | 0·3011 | 9·235 |
| 1·0832 | 20·0 | 0·4809 | 0·3009 | 9·232 |
| 1·0837 | 20·1 | 0·4807 | 0·3008 | 9·228 |
| 1·0841 | 20·2 | 0·4805 | 0·3007 | 9·224 |
| 1·0846 | 20·3 | 0·4803 | 0·3006 | 9·220 |
| 1·0850 | 20·4 | 0·4801 | 0·3005 | 9·216 |
| 1·0855 | 20·5 | 0·4798 | 0·3003 | 9·212 |
| 1·0859 | 20·6 | 0·4797 | 0·3002 | 9·209 |
| 1·0864 | 20·7 | 0·4795 | 0·3001 | 9·205 |
| 1·0868 | 20·8 | 0·4794 | 0·3000 | 9·201 |
| 1·0873 | 20·9 | 0·4791 | 0·2998 | 9·197 |
| 1·0877 | 21·0 | 0·4790 | 0·2997 | 9·194 |
| 1·0882 | 21·1 | 0·4787 | 0·2996 | 9·190 |
| 1·0886 | 21·2 | 0·4786 | 0·2995 | 9·186 |
| 1·0891 | 21·3 | 0·4783 | 0·2993 | 9·182 |
| 1·0895 | 21·4 | 0·4782 | 0·2992 | 9·179 |
| 1·0900 | 21·5 | 0·4779 | 0·2991 | 9·174 |
| 1·0904 | 21·6 | 0·4778 | 0·2990 | 9·171 |
| 1·0909 | 21·7 | 0·4775 | 0·2988 | 9·167 |
| 1·0914 | 21·8 | 0·4773 | 0·2987 | 9·163 |
| 1·0918 | 21·9 | 0·4772 | 0·2986 | 9·159 |
| 1·0923 | 22·0 | 0·4769 | 0·2984 | 9·155 |
| 1·0927 | 22·1 | 0·4768 | 0·2983 | 9·151 |
| 1·0932 | 22·2 | 0·4765 | 0·2982 | 9·148 |
| 1·0936 | 22·3 | 0 4764 | 0·2981 | 9·144 |
| 1·0941 | 22·4 | 0·4762 | 0·2980 | 9·140 |
| 1·0945 | 22·5 | 0·4760 | 0·2979 | 9·137 |
| 1·0950 | 22·6 | 0·4758 | 0·2977 | 9·132 |
| 1·0954 | 22·7 | 0·4756 | 0·2976 | 9·129 |
| 1·0959 | 22·8 | 0·4754 | 0·2974 | 9·125 |
| 1·0964 | 22·9 | 0·4752 | 0·2973 | 9·121 |
| 1·0968 | 23·0 | 0·4750 | 0·2972 | 9·117 |
| 1·0973 | 23·1 | 0·4748 | 0·2971 | 9·113 |
| 1·0977 | 23·2 | 0·4746 | 0·2970 | 9·110 |
| 1·0982 | 23·3 | 0·4744 | 0·2968 | 9·106 |
| 1·0986 | 23·4 | 0·4742 | 0·2967 | 9·102 |
| 1·0991 | 23·5 | 0·4740 | 0·2966 | 9·098 |
| 1·0966 | 23·6 | 0·4738 | 0·2965 | 9·094 |
| 1·1100 | 23·7 | 0·4736 | 0·2963 | 9·091 |

# PROCEEDINGS OF SOCIETIES.

## MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

*Ordinary Meeting, February 22nd, 1887.*

Professor OSBORNE REYNOLDS, LL.D., F.R.S., Vice-President, in the Chair.

"*On the Delicacy of Spectroscopic Reaction in Gases.*' By T. W. BEST. Communicated by Dr. ARTHUR SCHUSTER, F.R.S.

Seeing that very minute quantities of a great many bodies can be detected with ease in the spectroscope, at the request of Sir Henry Roscoe the following experiments were undertaken with the view of testing the efficiency of the spectroscope as a means for ascertaining the purity of gases.

The three gases, hydrogen, nitrogen, and oxygen, only were experimented upon: thus the smallest amount of hydrogen, whose spectrum could be observed in that of nitrogen, and *vice versa*, was first determined; and then the smallest amount of nitrogen in oxygen, and oxygen in nitrogen respectively, at the atmospheric pressure.

*Apparatus used.*

1. Spectroscope. 2. Induction coil. 3. Eudiometer.

1. The collimator, prism stage, and telescope of the spectroscope were mounted on separate stands; only one prism was used whose angle is 59° 33′, and the magnifying power of the telescope is 26·9.

Only about a quarter of the length of the spectrum could be seen in the spectroscope at once, and there being no scale the position of the lines sought after had to be measured from known gas lines, by a micrometer screw and pointer attached to the eyepiece.

2. An induction coil was used with a small Leyden jar

in the circuit to obtain the spectrum. Under ordinary conditions the length of spark in air, with jar in circuit, was 1·5 c.m., while without the jar a spark = 5·2 c.m. in length could be obtained.

3. Two eudiometers were used, 70 c.m. long, 1·9 c.m. wide, graduated up to 160 c.c., and having aluminium electrodes 0·25 c.m. apart sealed into the side at a distance of 30 c.m. from the bottom; the tap at the top serving to let in, from a burette, the required amount of gas.

To get rid of all the air the eudiometer was filled with mercury, by exhausting the air above it with a water-pump.

In most cases when the spectrum was observed the gases were under a pressure reduced by 1 inch of mercury, —*i.e.*, the mercury stood about 1 inch higher in the tube than in the trough.

Unless specified to the contrary the gases were thoroughly dried by standing for a few hours over phosphoric anhydride.

The phosphoric anhydride was rammed tightly into a small tube which can be slipped into the eudiometer through the mercury, a hole being bored through the mass of $P_2O_5$ to allow the mercury to run off the top of it, and thus expose its surface to the gas.

Each gas had its own tube of $P_2O_5$, so that each tube of $P_2O_5$ did not become contaminated with more than one gas.

Experiments were tried with—

(*a*) Nitrogen in hydrogen.
(*b*) Hydrogen in nitrogen.
(*c*) Nitrogen in oxygen.
(*d*) Oxygen in nitrogen.

### (*a*) *Nitrogen in Hydrogen.*

The hydrogen was generated by the action of sulphuric acid on zinc, washed and dried by passing through water and strong sulphuric acid, and after coming off for some time was collected over mercury.

The eudiometer is then placed in front of the spectroscope slit (at a distance of ½ metre), the spark focussed on to the slit by means of a small lens, and the spectrum examined.

If nitrogen or oxygen are not visible, and only the three hydrogen bands are present, then air (or, in some experiments, pure nitrogen) is added to the hydrogen in small quantities (about 1 c.c.) at a time, and the spectrum observed between each addition.

Thus, in one case, to 143 c.c. hydrogen was added to 1 c.c. air and the nitrogen lines were not visible, so another 1 c.c. air was added; but now the nitrogen green line wave-length 5004 was seen very faintly, and on the addition of another 1 c.c. air it could easily be seen. Therefore the amount of nitrogen that must be present in hydrogen in order to be detected in the spectroscope is 1·1 per cent.

Again, to 130 c.c. hydrogen 1 c.c. pure nitrogen (made by passing air over thin sticks of phosphorus in Hempel's gas analysis bulbs) was added, from a Hempel's burette, but the nitrogen line was not seen; so 0·5 c.c. more nitrogen was added, and now the nitrogen green line was seen, but it was rather faint. This gives 1·1 per cent.

To another 130 c.c. hydrogen, not dried at all, 1 c.c. nitrogen was added, but no nitrogen lines appeared; 0·6 c.c. more nitrogen was added, and the nitrogen line was then seen. This gives 1·2 per cent.

To 118 c.c. hydrogen, dried by having concentrated sulphuric acid in the eudiometer on the top of the mercury, 1 c.c. nitrogen was added, and the nitrogen line was not then visible: on addition of 0·2 c.c. more nitrogen the nitrogen line was not visible, but on addition of 0·2 c.c. more it came again into view. This gives 1·2 per cent. Mean of the four experiments is 1·15.

Therefore the amount of hydrogen that must be present in hydrogen to be detected in the spectroscope is 1·1 per cent.

Again, 4·5 c.c. nitrogen were added to 143 c.c. hydrogen, and the nitrogen line wave-length 5004 was easily seen; on adding 1 c.c. more nitrogen the yellow nitrogen lines wave-lengths 5681 and 5666 came out, and another green line wave-length 5164 makes its appearance on the addition of 2·5 c.c. more.

The result is not affected in the least, whether air pure nitrogen is added to the hydrogen.

### (*b*) *Hydrogen in Nitrogen.*

To 112 c.c. pure nitrogen (made by the method already given) 6·7 c.c. hydrogen were added, and the green and red hydrogen bands were distinctly visible.

To 144 c.c. nitrogen 1·6 c.c. hydrogen were added, and the green band became visible, not as a band, but as a very broad, thick line, quite sharp at the edges, and on the addition of more hydrogen it widened out into a band. The red hydrogen band was also visible at this time as a broad line.

To 140 c.c. nitrogen 0·35 hydrogen was added; the red hydrogen band was easily seen, but the green band only flashed in occasionally as a broad line. On addition of 0·3 c.c. more hydrogen it was still a broad line, and broadened out into a band on adding more hydrogen.

Therefore the amount of hydrogen that must be present in nitrogen in order that the green band in its spectrum may be observed in the spectroscope is 0·25 per cent.

### (*c*) *Nitrogen in Oxygen.*

The oxygen was made by decomposing potassium chlorate, passing the gas through NaOH and $H_2SO_4$, and collecting over mercury, as usual.

To 153 c.c. oxygen 2·9 c.c. nitrogen were added, and the nitrogen green line wave-length 5004 was visible.

To 132 c.c. oxygen 2 c.c. nitrogen were added, and the nitrogen line was again seen. The gas was not dried in the above two experiments at all.

To 130 c.c. oxygen 1 c.c. nitrogen was added, and the nitrogen line was seen, but it was very faint. This gives 0·78 per cent.

To 128 c.c. oxygen 0·6 c.c. nitrogen was added, and the nitrogen line was not seen; on adding 0 8 c.c. more nitrogen the green nitrogen line wave-length 5004 was visible, and on addition of 0·3 c.c. more nitrogen it could easily be seen.

Therefore the smallest amount of nitrogen that must be present in oxygen in order to be detected in the spectroscope is 0·8 per cent.

### (*d*) *Oxygen in Nitrogen.*

To 127 c.c. nitrogen 30 c.c. air had to be added before the oxygen blue line wave-length 4648 became visible. This gives 4·7 per cent.

To 108 c.c. nitrogen 22·6 c.c. air were added before the oxygen line became visible. This gives 4·5 per cent.

To 104 c.c. nitrogen 5 c.c. oxygen were added, and the oxygen line was seen very easily.

To 138 c.c. nitrogen 4 c.c. oxygen were added, and the oxygen line was not visible, but on adding 3 c.c. more oxygen it could be seen easily. This gives 4·4 per cent. In the last two experiments the gas was not dried at all.

Therefore the amount of oxygen that must be present in nitrogen in order to be detected in the spectroscope is 4·5 per cent.

The addition of air to the oxygen gives the same result as adding pure nitrogen to the oxygen, so that it is immaterial which is used; neither does the dryness of the gas seem to affect the results.

The following experiments were made at diminished pressures, to see how the above results are affected at different pressures:—

Thus, to 95 c.c. hydrogen, at 11 inches mercury pressure, 1·5 c.c. air was added, and the nitrogen line was just visible. Now 95 c.c. hydrogen at 11 inches pressure = 35 c.c. at 30 inches pressure, and this gives 3·5 per cent nitrogen.

Again, to 90 c.c. at 10 inches pressure were added—

0·5 c.c. air, and no nitrogen lines were visible.
0·3 c.c. air more, ,, ,, ,,
0·4 c.c. air more, ,, ,, ,,
0·2 c.c. air more, and nitrogen line became visible.

Therefore 1·4 c.c. air in 30 c.c. hydrogen = 3·7 per cent nitrogen.

Thus a diminution of pressure from 29½ inches to 10½ inches mercury alters the amount of nitrogen that must be present in hydrogen in order to be detected in the spectroscope from 1·1 per cent to 3·6 per cent.

96 c.c. hydrogen at 2 inches pressure *showed the three hydrogen bands as wide lines, sharp at the edges, the red being the broadest.* On the addition of 0·25 c.c. air the nitrogen line wave-length 5004 was seen at the edges of the field only, and not extending across.

On adding further small quantities of air (up to 3·8 c.c.) more nitrogen lines came into view, till at last they were all in view, but they were only visible at the edges of the field, and would not extend across the field. The hydrogen lines became broader on each addition of nitrogen, and ultimately they became bands. At the end of the experiment the pressure had increased to 2¾ inches mercury.

To 101 c.c. hydrogen at 3½ inches pressure—

0·04 c.c. air was added, but no nitrogen lines appeared.
0·16 c.c. air ,, ,, ,, ,,
0·26 c.c. air ,, ,, ,, ,,
0·1 c.c. air the nitrogen green line appeared at the edges only.
0·2 c.c. air the nitrogen green line became much clearer.

Thus 0·36 c.c. air = 0·29 nitrogen in 11·8 c.c. hydrogen = 2·5 per cent.

Therefore at 3½ inches of mercury pressure the smallest amount of nitrogen that must be present in hydrogen in order that it may be detected in the spectroscope is 2·5 per cent.

*Complete Results.*

| | | Per cent. | |
|---|---|---|---|
| *a.* | Nitrogen in hydrogen at atmospheric pressure, | 1·1 | N. |
| | Nitrogen in hydrogen at 10½ inches ,, | 3·6 | N. |
| | Nitrogen in hydrogen at 3½ ,, ,, | 2·5 | N. |
| *b.* | Hydrogen in nitrogen at atmospheric ,, | 0·25 | H. |
| *c.* | Nitrogen in oxygen ,, ,, | 0·8 | N. |
| *d.* | Oxygen in nitrogen ,, ,, | 4·5 | O. |

## NOTICES OF BOOKS.

*Joint Scientific Papers.* By JAMES PRESCOTT JOULE, D.C.L., F.R.S., &c. Published by the Physical Society of London. London: Taylor and Francis. 1887. Vol. II.

THE first paper in this volume is the joint work of Dr. Joule and the Rev. Wm. Scoresby, D.D., and is entitled "Experiments and Observations on the Mechanical Powers of Electro-Magnetism, Steam, and Horses."

The experiments consisted chiefly in causing armatures of special construction to revolve in front of steel magnets, by means of a current from a Daniell's battery: the current passing and the power developed were measured, and the maximum available duty of such an apparatus was found to be equal to 80 lbs. lifted 1 foot per grain of zinc consumed, or about half the theoretical maximum. These results are then compared with those obtained with two other sources of power, viz., steam and horses, from which it is found that a boiler and steam-engine in its most improved form is not able to convert more than one-tenth of the *vis viva* due to the combustion of coal into useful power. Similar observations of the power of a horse and the food it consumes show that only one-quarter of the *vis viva* generated by the food is converted into a useful mechanical effect, the remaining three-quarters being required to keep up the animal heat, &c.

The second paper is a very elaborate and laborious one, on "Atomic Volume and Specific Gravity," by J. P. Joule and Dr. Lyon Playfair, and extends over more than 200 pages. The importance of discovering the law which governs the volumes of solid and liquid substances has long been recognised, and has received considerable attention for some time past. Dr. Thomson was the first chemist who called attention to this subject, in the year 1831, and since then others—including Kopp, Schröder, and Persoz—have by their researches thrown considerable light on the matter.

Hitherto the enquiry has been principally confined to solid bodies; but the fact that they do not present matter in a uniform condition, free from cohesion, constitutes an objection to their use. The authors therefore thought it desirable to separate the particles so as to destroy their cohesion, without at the same time altering their chemical properties; they accordingly resolved to have recourse to solution in water as a means for effecting their purpose, and to experiment principally on soluble bodies of well-known constitution. It was of course necessary, at the same time, to determine the relation of the solid volume to the volume of the salt in solution, and also the specific gravities of the salts used, about which very little was known. An immense number of salts were tried and determined; they were divided into eight sections, such as nitrates, carbonates, oxalates, chromates, &c. The results of all these experiments are given in detail, and the various groups and sub-sections are given in tabulated form.

The laws which it is considered regulate the volumes of salts are summed up in the form of two propositions, as follows:—

PROP. I.—*Compounds dissolved in water increase its volume for every equivalent either by 9 or by multiples of 9.*

PROP. II.—*The volume occupied by a salt in the solid state has a certain relation to the volume of the same salt when in solution, and has also a fixed relation to the volume occupied by any other salt.*

Series II. deals with "The relation in volumes between simple bodies, their oxides, and sulphurets, and on the differences exhibited by polymorphous and allotropic substances." In this memoir the authors endeavour to confirm the multiple relation which was pointed out in the case of solid salts, and they commence with the volumes of the metallic elements. As in the previous experiments with salts in solution, the substances under experiment are divided into sections. Section I, deals with the specific gravities and volumes of the metallic elements; and the conclusions drawn from these experiments are that the metals, when obtained in a finely divided state, so as to be deprived of cohesion, and also when rendered fluid by heat, have volumes which are multiples of the unit 1·225, but the volumes of metals in the solid crystalline condition are, in general, multiples of a number about 1-20th less than 1·225. Then follow the sections on the oxides of the metals, the sulphurets, the non-metallic elements and their oxides, &c.

The results are announced generally under the following proposition:—

> "The volumes of solid bodies bear a simple relation to each other, being multiples of a sub-multiple of the volume of ice, which for convenience is adopted as a standard."

And after discussing this proposition at some length, the law is finally stated in these words:—

> "*The atomic volumes of bodies stand in a simple multiple relation to each other.*"

Series III. of these experiments is on the maximum density of water. This research was undertaken with a view to finding the best temperature at which to determine specific gravities, objection being made to the Conti-

nental standard, viz., freezing-point, and to 60° F. as generally adopted in our own country: water at 60° F. cannot be at the most desirable temperature, on account of its high rate of expansion at that point. The method employed for this determination is fully described, and after giving the results of many experiments it is finally decided that water is at its maximum density at a temperature of 39·1° F.

Series IV., on the expansion by heat of salts in the solid state, and Series V., on the disappearance of the volume of the acid, and in some cases of the base, in the crystals of highly hydrated salts, complete this valuable series of papers.

The latter part of the volume contains several papers, the joint labours of Dr. Joule and Sir Wm. Thomson, on "The Thermal Effects experienced by Air in Rushing through Small Apertures," and on "The Thermal Effects of Fluids in Motion." Mayer's hypothesis, that the heat evolved from compressed air kept at a constant temperature is the mechanical equivalent of the work done in compressing it, was verified by Joule as at least approximately true for air at ordinary temperatures, but it cannot be rigorously true except for one definite temperature. The experiments here recorded were undertaken to decide this point, but they are not considered altogether satisfactory on account of the apparatus being inadequate. If Mayer's hypothesis were true, air forced through a long pipe open wide at the end, but contracted considerably in one place, would have the same temperature after, as it had before reaching the narrow passage, but a cooling effect was always observed. Another form of contraction was tried, which consisted of a bit of calf-skin bound tightly over the end of the tube, the pores of the leather being found sufficient to allow the air to pass: as in the former case, the same cooling effect was observed, but, accidental circumstances interfering with the results, a more elaborate set of apparatus was put up, and the previous result—that air is cooled by being forced through a porous plug—was confirmed, though it was found that when issuing from a single orifice the *vis viva* of the rushing air is converted into heat.

A number of experiments are next described in which the substance used as the porous plug is changed, cotton, wool, silk, &c., being tried. Another series gives the results of substituting carbonic acid or hydrogen for air. The cooling effect experienced by hydrogen was at first found to be 1-13th of that observed with air, but subsequent experiments showed that a heating effect was obtained.

Other experiments were made, such as whirling thermometers or thermo-electric junctions through the air at a high speed, and a rise of temperature was always experienced.

The ultimate result of this research is that when the rush of the air is retarded by a porous plug, and allowed to expand, the actual temperature of that air is lower than before compression.

## CORRESPONDENCE.

### THE INSTITUTE OF CHEMISTRY.

*To the Editor of the Chemical News.*

SIR,—What has been the outcome of all the letters which appeared in the CHEMICAL NEWS about a year ago on the above subject; and what has the Manchester Committee, of which Mr. Wm. Thompson, F.C.S., was secretary, done in the matter? I feel sure there are many who would be interested to know in addition to myself—I am, &c.,

H. M. CARRINGTON.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 15, April 12, 1887.

**Examination of the Alkaline Vanadates.**—A. Ditte.—In this paper the author describes seven sodium vanadates, the neutral salt, $NaOVO_5$, $NaO_2VO_5$, $2NaO,3VO_5$, $NaO,3VO_5$, $2NaO,VO_5$, $3NaO,VO_5$, and $4NaO,VO_5$.

No. 16, April 18, 1887.

**On a Peculiar Circumstance of the Production of Sodium Hydrocarbonate.** — Paul de Mondésir.— The author has observed that sodium carbonate, if combined with a single equivalent of water, absorbs carbonic acid at ordinary temperatures extremely slowly, if at all. On the contrary, if it is mixed with a small proportion of dry bicarbonate, the reaction sets in at once, and with an energy proportionate to the quantity of bicarbonate. This is a case of a solid being "primed" by a solid.

**Researches on the Barium Phosphates. Application to Acidimetric Analysis.**—A. Villiers.—It is known that phosphoric acid behaves with phenol-phthalein like a bibasic acid. It may be determined by a simple volumetric operation by means of a standard solution of potassa or of baryta water. In the first case there is formed an alkaline phosphate, neutral to phenol-phthalein; in the second case an insoluble barium diphosphate, and the end of the reaction is clearly indicated. Hence it seems that the acidimetric determination of an acid, such as the sulphuric, hydrochloric, acetic, &c., should be effected without difficulty, and it is in reality so if we operate with a standard solution of potassa. With baryta-water the case is different. If, after having saturated a certain volume of hydrochloric acid with baryta-water, in presence of phenol-phthalein, we add sodium diphosphate, the addition of this substance, neutral or rather slightly alkaline, to phenol-phthalein produces the same effect as the addition of an acid and a further quantity of baryta-water is necessary to effect saturation.

**Method of Determining the Relative Value of the Four Units of Chemical Action of the Carbon-Atom.**—Louis Henry.—The identity or the difference of value of the four units of affinity of carbon may be deduced from the nature of the monocarbides $CX_4$. Whatever may be the relative value of the different units of affinity, the simple monocarbide derivatives, $CX_4$, containing only radicles of the same sort fixed upon the carbon nucleus, must be unique, each in its species. It is thus in reality; we only know the compounds $CH_4$, $CCl_4$, $CO_2$, $CS_2$, $C(OC_2H_5)_4$, &c., under a single form; but it must be different with the mixed compounds, where different radicles are fixed upon the carbon atom. If these four units of affinity are of the same sort, and have the same value, the mixed derivatives ought to be also each unique in its species; but they ought to exist in different forms if these units of affinity are not identical. Let us take the simplest case and suppose one unit of affinity different from the three others; this being the case a double compound, $CX_3X'$ ought to form two distinct varieties; a triple compound, $CX_2X'X''$, will form three, and a quadruple compound, $CXX'X''X'''$, will constitute four. We see the question returns to the study of isomerism in the mixed monocarbon derivatives. The author has hitherto obtained, both for acetonitrile and for nitromethane, the derivatives $\alpha$, $\beta$, and $\gamma$, and he has not been able to find among these derivatives of different substitutive orders any appreciable difference.

**Products of the Fermentation of Sugar by the Elliptical Yeast.**—Ed. Claudon and E. C. Morin.—The authors have submitted to the action of the elliptical

yeast 100 kilos. of sugar. The yeast was obtained from the lees of a white wine of Rouillac (Charente) of the vintage of 1885. The product of the fermentation possessed a vinous odour, very distinct from the odour presented by a similar wort fermented by beer yeast. The products obtained were :—

| | |
|---|---|
| Aldehyd .. .. .. .. .. | traces |
| Ethylic alcohol .. .. .. | 50615·0 grms. |
| Normal propylic alcohol .. | 2·0 |
| Isobutylic alcohol .. .. .. | 1·5 |
| Amylic alcohol .. .. .. | 51·0 |
| Œnanthic ether .. .. .. | 2·0 |
| Isobutylene-glycol .. .. .. | 158·0 |
| Glycerin .. .. .. .. .. | 2120·0 |
| Acetic acid .. .. .. .. | 205·3 |
| Succinic acid .. .. .. .. | 452·0 |

The authors call attention to the small proportion of the higher alcohols formed in this fermentation, the absence of the bases of fusel oils, as well as of normal butylic alcohol and of butyric acid.

## MISCELLANEOUS.

**University College, Nottingham.**—At a University College Committee recently held, Professor F. Clowes, D.Sc., was unanimously appointed Principal for the ensuing year.

**Electrical Communication between Lightships and the Shore.**—The problem of effectually establishing electrical communication between our various lightships round the coast and the shore has, for a long time, occupied the attention of practical electricians and sailors, but for one reason or another none of the methods tried have met with success, generally owing to the electric cable fouling the mooring chains as the ship swings round with the tide. The latest scheme for effecting this communication is the one recently patented by Messrs. Little and Hale. The method adopted by them is to moor the lightship, by means of a compound universal swivel joint, to the centre-boss of a specially constructed anchor, or rather set of four mushroom anchors, whose shanks are all connected at the hub, while the outer ends are encircled by a large rim or "crinoline," the whole having somewhat the appearance of a huge massive wheel. The electric cable enters the crown of one of the mushrooms, and, passing along the shank, is led through a stuffing box to the interior of the boss, where two suitable rubbing contacts enable electrical communication to be maintained in whatever position the lightship may be, and thence through another stuffing box to the ship, without the possibility of its being fouled or twisted. The joints are made perfectly watertight by means of indiarubber packing rings, and all moving parts are bushed with phosphor-bronze. This method has the advantage of being extremely simple as well as thoroughly effective, and the inventors will no doubt have an opportunity before long of practically demonstrating the value of their invention.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

**Quinine Estimation.**—The published processes, as far as I am acquainted with them, are unsatisfactory. I should be glad to be informed of the methods used by quinologists of assaying cinchona bark. Does the quinine in their reports include amorphous as well as crystallisable alkaloid ?—PUZZLED.

**Watermark in Paper.**—There is no satisfactory chemical method of putting a watermark into paper after manufacturing. It must be done by a mechanical process; *e.g.*, imitation watermarks may be made in paper by pressure upon a marked plate in which the watermark is raised. Of course they cannot be made as permanent as the real mark, as in that case the paper is thin under the mark.—J. H. SWINDELLS.

## MEETINGS FOR THE WEEK.

MONDAY, 9th.—Society of Arts, 8. (Cantor Lectures). "The Chemistry of Substances taking part in Putrefaction and Antisepsis," by J. M. Thomson, F.C.S.
TUESDAY, 10th.—Institution of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
—— Royal Institution, 3. "Electricity," by Prof. W. E. Ayrton, F.R.S.
—— Society of Arts, 8. "The Architecture of London Streets," by E. J. Tarver, F.S.A.
WEDNESDAY, 11th.—Society of Arts, 8. "Cottage Industries in Ireland," by Mrs. Ernest Hart.
—— Geological, 8.
—— Microscopical, 8.
THURSDAY, 12th.—Royal, 4.30.
—— Telegraph Engineers, 8.
—— Royal Institution, 3. "The Chemistry of the Organic World," by Prof. Dewar, F.R.S.
FRIDAY, 13th.—Royal Institution, 9. "Some Electrical Fishes," by Prof. J. S. Burdon Sanderson, M.D., F.R.S.
—— Quekett Club, 8.
SATURDAY, 14th.—Royal Institution, 3. "Victorian Literature," by Prof. John W. Hales, M.A.
—— Physical, 3. "A Modification of a Method of Maxwell's for Measuring the Coefficient of Self-Induction." by Mr. Ernest C. Rimington. "Note on Transformers for Electrical Distribution," by Prof. S. P. Thompson, D.Sc.

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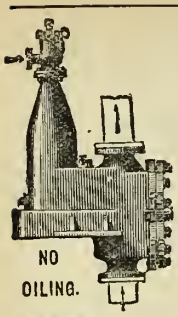

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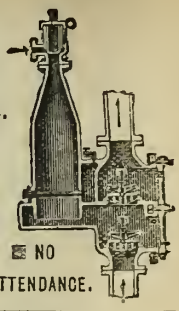
| 4 | 8,000 | 27 10 0 |
| 5 | 11,200 | £35 0 0 |
| 6 | 15,200 | 42 10 0 |
| 7 | 25,000 | 65 0 0 |

NO OILING.



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|---|---|---|---|---|
| 1 | 25 | 5 0 0 | 8 0 0 | 8 10 0 |
| 2 | 40 | 7 0 0 | 9 0 0 | 11 10 0 |
| 3 | 80 | 9 0 0 | 14 0 0 | 17 10 0 |
| 4 | 160 | 12 0 0 | 18 0 0 | 23 0 0 |
| 5 | 250 | 15 0 0 | 22 10 0 | 31 0 0 |
| 6 | 320 | 18 0 0 | .. | .. |
| 7 | 400 | 21 0 0 | .. | .. |
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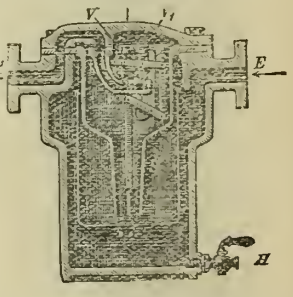
| „ Lead .. .. | 2 10 | 3 0 | 3 10 | 4 10 | 5 10 | 7 0 | 10 |
| „ Brass .. .. | 3 0 | 3 15 | 4 5 | 5 0 | 6 0 | 8 0 | 11 |
| „ Porcelain .. | 5 0 | 6 0 | 7 0 | 8 0 | 9 0 | .. | .. |

**KÖRTING'S PATENT STEAM TRAP.**




The water is discharged continuously, and not intermittently as in others.

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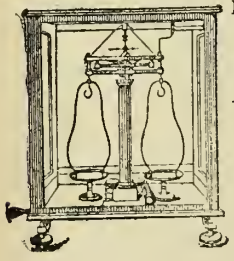

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THE CHEMICAL NEWS.

Vol. LV. No. 1433.

## ON AUSTRALIAN BAT GUANO AND SOME MINERALS OCCURRING THEREIN.

By R. W. EMERSON MACIVOR, F.I.C., F.C.S., F.R.G.S., &c.,
Late "Clarke" Lecturer on Agricultural Chemistry, Victoria, and Principal of the Department of Agriculture, Technical College, Sydney, N.S.W.

In caves situated in different parts of Victoria there exist more or less extensive deposits of guano, which are generally believed to have been formed from the excrements and other remains of bats. Some of these accumulations have little or no commercial value, while in others the guano contains sufficient nitrogen and phosphoric acid to entitle it to rank with useful fertilisers. The following are analyses of some inferior qualities :—

| | Hamilton. | Portland. | Warrnambool. (1). | Warrnambool. (2). |
|---|---|---|---|---|
| Water .. .. .. | 35·71 | 19·97 | 20·30 | 37·48 |
| Organic matter .. | 33·77 | 41·33 | 8·95 | 18·30 |
| Ash .. .. .. | 30·52 | 38·70 | 70·75 | 44·22 |
| | 100·00 | 100·00 | 100·00 | 100·00 |
| Total nitrogen .. | 1·08 | 1·28 | 0·91 | 1·89 |
| Phosphoric acid.. | 2·41 | 11·88 | 7·45 | 9·98 |

The samples from Hamilton and Portland fairly represented the average of the contents of the caves. In the case of the Warrnambool guano the first sample was taken from near the surface at the entrance of the cave, and the second from a depth of four feet in the centre of the deposit in the same cave. This guano, as obtained from the depth mentioned, has distributed throughout its mass, though only very sparingly, minute glistening particles of a mineral presently to be noticed, viz. *Newberyite*.

But the only important deposits of bat guano yet discovered in Australia are those in the Skipton caves on the estate of the Hon. Francis Ormond, about thirty miles south-west of the city of Ballarat. The bottom of each of these extensive basaltic caverns is covered with the guano to a depth of thirty feet in some places, and the origin of the deposits is pretty well indicated by the fact that until lately myriads of bats made the caves their home during daylight, and could be seen hanging in countless clusters from the roof.

The Skipton guano varies very much in appearance and composition. In the older and drier deposits it is light brown in colour, nearly odourless, and contains white nodular phosphate of magnesium and ammonium disseminated throughout its body together with fine colourless or slightly tinted prismatic crystals of the mineral which I in 1878 named *Hannayite*—

$$[Mg_2H_2(PO_4)_2.Mg_2H_2(NH_4)_2(PO_4)_2+8H_2O]$$

in honour of my friend Mr. J. B. Hannay, and rhombic crystals of another mineral which I in the same year called *Newberyite* $[Mg_2H_2(PO_4)_2+6H_2O]$ in compliment to Mr. J. Cosmo Newbery, C.M.G., the well-known Australian chemical authority. The great bulk of these deposits, however, consists of dark brown or brown-black guano containing so much water that when dug out it comes away in lumps, whereas the older deposits are powdery. This moist, or I should say wet, material is thickly studded with large and often perfect crystals of *Struvite* $[Mg_2(NH_4)_2(PO_4)_2+12H_2O]$.

In the following table I have arranged some analyses of Skipton guano after the removal of all crystals of the minerals mentioned :—

| | I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|
| Water .. .. .. | 16·74 | 30·52 | 30·96 | 33·50 | 44·50 |
| Organic matter .. | 22·00 | 44·98 | 31·21 | 44·66 | 32·60 |
| Ash .. .. .. | 61·26 | 24 50 | 37·83 | 21·84 | 22·90 |
| | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |
| Total nitrogen .. | 2·40 | 4·51 | 5·05 | 6·95 | 3·8 |
| Nitrogen as nitric acid .. .. .. | 0·39 | 0·87 | 1·26 | 1·34 | 0·46 |
| Phosphoric acid, $P_2O_5$.. .. .. | 7·64 | 4·10 | 10·87 | 3·61 | 7·80 |

I. Sample was light in colour and contained neither *Struvite* nor *Hannayite*, but only *Newberyite*, and amorphous phosphate of magnesium and ammonium.

II., III., and IV. Samples had a rich brown colour, and contained much *Struvite* and also some *Hannayite*. *Newberyite* was absent in each case.

V. Sample was brown-black, and full of *Struvite*, but neither of the other minerals was present. All the samples contained nitrates. The ash was found to contain only traces of sulphate and carbonate of calcium, and to be composed of siliceous matter, oxide of iron, traces of manganese, phosphates of magnesium and calcium, chloride of sodium, and a little potassium.

When treated with water the guano gives up a considerable part of its phosphoric acid and nitrogen, together with organic matter, yielding a dark brown solution. This solubility indicates the fitness of the manure for top-dressing grass-land and young cereals, and extensive field trials made under my direction in various parts of the colony gave eminently satisfactory results. If any objection could be urged against the guano, it would be on the score that its first effect on tender plants is of a "too forcing" character.

Turning from the consideration of the guano to the minerals that occur in it, I may mention that the crystallographic characters of *Struvite*, *Hannayite*, and *Newberyite* have been most minutely examined by Professors vom Rath, of Bönn, and G. Ulrich, of the University of New Zealand, to both of whom I sent some excellent specimens. The results obtained by these gentlemen are to be found in the latest edition of Dana's "Mineralogy, so that I need not here further refer to them.

*Struvite*.—Analyses of this mineral have already been published by Ulex and by J. C. Newbery, but the following results may not be wholly uninteresting :—

| | Found. | Theory. |
|---|---|---|
| Magnesium oxide.. .. | 16·069 | 16·327 |
| Ferrous ,, .. .. | 0·810 | — |
| Manganous ,, .. .. | 0·163 | — |
| Ammonium ,, .. .. | 10·567 | 10·612 |
| Phosphoric ,, .. .. | 28·819 | 28·980 |
| Water (as difference) .. | 43·572 | 44·081 |
| | 100·000 | 100·000 |

When exposed for a long time to the air crystals of struvite lose some of their water of crystallisation, and become thinly coated with a white powder. The nodular phosphate of magnesium and ammonium in the guano of the older deposits is in my opinion only altered struvite

*Hannayite*.—Crystals of *Hannayite* do not lose water by exposure to the atmosphere or to a temperature of 100° C. At 110° to 115°, however, they give up about two-thirds of their water of crystallisation, and lose their transparency. When heated over a Bunsen the crystals swell considerably, become opaque, and ultimately assume peculiar "maggot-like" forms. The residue is soluble in nitric acid, but only partially in hydrochloric acid, proving it to contain pyro- and meta-phosphates of magnesium—

$$Mg_2H_2(PO_4)_2.MgH_2(NH_4)_2(PO_4)_2 = Mg_2P_2O_7+Mg(PO_3)_2+2NH_3+2H_2O.$$

The crystals of this mineral are frequently found adhering to those of *Struvite* in such a way as almost to in-

dicate that they had been formed from the latter. Further, I may mention that *Hannayite* occurs most abundantly in guano containing the nodular double phosphate already referred to, and no distinct crystals of *Struvite*. The following is an analysis of *Hannayite*:—

| | Found. | Theory. |
|---|---|---|
| Magnesium oxide.. .. | 18·545 | 18·869 |
| Ferrous ,, .. .. | 0·310 | — |
| Manganous ,, .. .. | 0·087 | — |
| Ammonium ,, .. .. | 8·095 | 8·176 |
| Phosphoric ,, .. .. | 44·711 | 44·654 |
| Water (as difference) .. | 28·252 | 28·301 |
| | 100·000 | 100·000 |

*Newberyite.*—It is extremely difficult to free this mineral from the guano that exists locked up in the body of the crystal. However, I succeeded in getting a sufficient quantity of pure substance to make an analysis:—

| | Found. | Theory. |
|---|---|---|
| Magnesium oxide.. .. | 22·368 | 22·988 |
| Ferrous ,, .. .. | 0·850 | — |
| Manganous ,, .. .. | 0·206 | — |
| Phosphoric ,, .. .. | 40·728 | 40·805 |
| Water (as difference) .. | 35·838 | 36·207 |
| | 100·000 | 100·000 |

The crystals do not part with water at 100° C., but lose the whole six molecules at about 170° C., and on ignition leave pyrophosphate only.

I may, in conclusion, mention that two other phosphates of magnesium and ammonium new to science exist in Skipton guano, and these I have named *Muellerite* and *Dittmarite* respectively. I propose to make these minerals the subject of a future paper.

## SHORT TITLES OF CHEMICAL PERIODICALS CURRENT IN 1887.

By H. CARRINGTON BOLTON.

[For full titles and bibliographical details see "*Catalogue of Scientific and Technical Periodicals*, 1665—1882," by Henry Carrington Bolton, Smithsonian Institution, Washington, 1885, pp. x—774, 8vo.]

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Bulletin de l'association des chimistes de sucrerie et de distillerie de France et des colonies. 8vo. Paris. (Established in 1883.)

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Meddelelser fra Carlsberg laboratoriet. Christiania. (Established in 1884.)

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Orosi (L'), Giornale di chimica. Firenzi. (Established in 1878.)

Ragguagli. Laboratorio chimico-agrario di Perugia. Perugia. (Established in 1883.)

Recueil des travaux chimiques des Pays-Bas. Leide. (Established in 1882.)

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Vierteljahresschrift über die Fortschritte auf dem Gebiete der Chemie der Nahrungs- und Genussmittel. Berlin. (Established in 1886.)

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Zhurnal russkova khimicheskova i fizicheskova. St. Petersburg. (Established in 1869.)—*Journal of Analytical Chemistry*, Vol. i., Part 2, April, 1887.

## REMARKABLE SPECIFIC GRAVITY OF LIME-WATER.

By J. ALFRED WANKLYN.

I have recently had occasion to take the specific gravity of lime-water, and have noted a peculiarity which appears to me to be of very great interest. According to a recent determination in my laboratory a litre of lime-water contains 1·344 grms. of CaO, and the specific gravity of the lime-water reaches the extraordinary figure 1002·35, compared with distilled water at the same temperature, reckoned as 1000·00 (the temperature was 13° C.).

It follows from these observations that in the formation of lime-water a most extraordinary contraction takes place.

Before solution :—

| | | |
|---|---|---|
| CaO .. .. | 0·5 c.c. = | 1·344 grms. |
| $H_2O$ .. .. | 1001·0 ,, = | 1001·0 ,, |

which contract so as to occupy one litre.

The contraction is, therefore, three times the volume of the lime which dissolves in the water and forms lime-water.

The purity of the lime-water was ascertained by exactly precipitating the lime by means of its equivalent of oxalic acid, filtering, and evaporating the filtrate to dryness; the residue was so small as to be insignificant.

Royal Institution of Great Britain.—Mr. John W. Hales, Professor of English Literature at King's College, will give the first of a Course of four lectures on Victorian Literature at the Royal Institution, on Saturday, May 14; and Mr. Victor Horsley, F.R.S., will give the first of a Course of three lectures on The Modern Physiology of the Brain and its Relation to the Mind, on Tuesday, May 17.

## THE HARDNESS OF METALS.*

By THOMAS TURNER, Assoc. R.S.M., F.C.S.,
Lecturer on Metallurgy, Mason College, Birmingham.

(Concluded from p. 207.)

### Part III.

It now remains to give an account of some results obtained by the form of instrument just described. It was thought it would be of interest in the first place to approximately calibrate the apparatus by comparison with a few substances of known hardness. Dr. Lapworth was good enough to select a few minerals for me, the specimens being considered pretty characteristic. Each specimen was examined on more than one face, and in two directions, at right angles to each other, on each surface. The values given therefore approximately represent the mean hardness of the specimens examined. In calcite considerable differences were noticed in the hardness of the faces employed. A few common metals were also tested, and for comparison several varieties of iron and steel are added, the results being given in Table A. It may be mentioned that my present apparatus was designed for use with cast-iron, and hence in the lower numbers the percentage error is probably greater than in the cases when 20 grms. or upwards was employed. I am hoping, however, shortly to have a modified instrument for softer substances, with which to carry on the investigation, and to examine various alloys used in the arts.

An examination of Table A shows that the weights used correspond closely in order with what might be anticipated from the hardness according to Moh's scale. The values obtained for the various minerals are considerably higher than those given by Franz, but, as previously shown, this, in all probability, depends on a different method of observation.

Table A.

| Substance. | Moh's scale. | Weight in grms. |
|---|---|---|
| Steatite .. .. .. .. .. .. | 1 | 1 |
| Lead (commercial) .. .. .. .. | 1½ | 1 |
| Tin lead alloy (66% Sn) .. .. .. | — | 2 |
| Tin (commercial) .. .. .. .. | 2 | 2½ |
| Rocksalt .. .. .. .. .. .. | 2 | 4 |
| Zinc (pure, annealed) .. .. .. | 2½ | 6 |
| Copper (pure, annealed) .. .. .. | 2½ | 8 |
| Calcite .. .. .. .. .. .. .. | 3 | 12 |
| Softest iron tested .. .. .. .. | — | 15 |
| Fluor-spar .. .. .. .. .. | 4 | 19 |
| Mild steel usually .. .. .. .. | 4—5 | 21 |
| Tyre steel .. .. .. .. .. .. | 4—5 | 20—24 |
| Good soft cast-iron .. .. .. .. | 4—5 | 21—24 |
| South Staffordshire bar iron .. .. | 4—5 | 24 |
| Apatite.. .. .. .. .. .. .. | 5 | 34 |
| Hard cast scrap .. .. .. .. .. | — | 36 |
| Window glass .. .. .. .. .. | 5—6 | 60 |
| Hardest cast-iron tested .. .. .. | — | 72 |

In Table B are reproduced my original experiments on the hardness of cast-iron as affected by the addition of silicon to white iron. (*Jour. Chem. Soc.*, 1885, p. 904). The effects here observed have recently been largely applied in England, Scotland, France, and elsewhere, in the production of a soft iron, with considerable tenacity, by the addition of silicon to a hard material, and already many thousands of tons of castings have been successfully prepared in this manner. An examination of Table B shows that the hardness as observed by means of a weighted diamond agrees very closely indeed with the working qualities, as given by an experienced workman. Further it will be seen that the tensile strength and hardness do not agree, but appear to follow almost in inverse order. These facts prove conclusively that *the method employed is capable of distinguishing between tenacity and hardness.*

* Read before the Birmingham Philosophical Society, Dec 9, 1886,

TABLE B.

*Influence of Silicon on the Hardness and Tenacity of Cast Iron.*

| No. | Silicon per cent. | Tensile Strength. | Hardness. |
|---|---|---|---|
| 1. | 0·19 | 10·14 tons | 72 |
| 2. | 0·45 | 12·31 ,, | 52 |
| 3. | 0·96 | 12·72 ,, | 42 |
| 4. | 1 96 | 15·70 ,, | 22 |
| 5. | 2·51 | 14·62 ,, | 22 |
| 6. | 2·96 | 12·23 ,, | 22 |
| 7. | 3·92 | 11·28 ,, | 27 |
| 8. | 4·75 | 10·16 ,, | 32 |
| 9. | 7·37 | 5·34 ,, | 42 |
| 10. | 9·80 | 4·75 ,, | 57 |

*Working Qualities.*

No. 1.—Very hard indeed.
,, 2.—Very hard, though not so hard as No. 1.
,, 3.—Hard, though softer than No. 2.
,, 4.—Good, sound, ordinary, soft-cutting iron, of excellent quality.
,, 5.—Rather harder than No. 4.
,, 6.—Like No. 4.
,, 7.—Like No. 6, but rather harder.
,, 8.—Rather harder than No. 7, though not unusually hard.
,, 9.—Still harder, cutting very like No. 10.
,, 10.—Hard-cutting iron, though still softer than No. 1.

TABLE C.

*Cast-Iron Specimens at Rosebank Foundry.*

| No. | Tensile Strength. | Relative Hardness. |
|---|---|---|
| 1 | 18·2 | 24 |
| 2 | 17·1 | 24 |
| 3 | 17·0 | 24 |
| 4 | 16·8 | 20 |
| 5 | 16 4 | 28 |
| 6 | 14·7 | 46 |
| 7 | 14·2 | 25 |
| 8 | 13·0 | 21 |
| 9 | 13 | 21 |
| 10 | 13 | 39 |
| 11 | 13 | 42 |
| 12 | 12½ | 18 |
| 13 | 12¼ | 18 |
| 14 | 12¼ | 21 |
| 15 | 12 | 35 |
| 16 | 11¾ | 49 |
| 17 | 10½ | 18 |
| 18 | 9¼ | 42 |
| 19 | 8½ | 25 |
| 20 | 8 | 25 |
| 21 | 7·8 | 21 |
| 22 | 6·5 | 25 |
| 23 | 6·5 | 25 |

In Table C are given the results of other experiments on the hardness of cast-iron, conducted last summer at the Rosebank Foundry, Edinburgh. The first four specimens have been preserved, and have been recently re-examined. In the other cases, however, the experiments were conducted in a room with unfavourable light, and with an apparatus which has been since improved. Had opportunity offered, therefore, these specimens would have been tested again, but unfortunately they were destroyed at the works soon after our experiments were finished. The numbers are, therefore, probably not so rigidly exact as in other cases, though, doubtless, quite sufficiently near to be of practical value. In his table we have a large number of specimens purposely selected so as to embrace as wide a range in tenacity as possible, and including, I believe, in the first five specimens, the highest recorded tensile strengths for British cast-iron. It will be seen that we have practically the same hardness with the highest as with the lowest tensile strength, and that in this case also no definite connection can be shown to exist between hardness and tenacity. Founders are usually of opinion that cast-iron can be made strong if it is made sufficiently hard. This is merely an old superstition, and the sooner it is exploded and forgotten the better for all concerned. So far as my experience has gone, it is quite the contrary. As a matter of fact, specimens with exceptionally high tensile strength are almost always good soft working irons; while special softness or unusual hardness is generally a sign of weakness.

TABLE D.

*Purest Bessemer Metal, with Small Quantities of Silicon Added.*

| No. | Tensile Strength. | Elongation per cent on 10 inches. | Hardness. |
|---|---|---|---|
| 1 | 21·80 | 24·7 | 18 |
| 2 | 20·72 | 19·5 | 16 |
| 3 | 22·60 | 15·4 | 17 |
| 4 | 23·18 | 15· | 17 |
| 5 | 24·23 | 24·0 | 20 |
| 6 | 27·45 | 12·8 | 21 |
| 7 | 25·77 | 22·0 | 20 |
| 8 | 21·89 | 24·2 | 15 |

Leaving cast-iron, we come to the consideration of the various varieties of soft steel. In Table D we have the results obtained with the purest iron obtainable in commerce, namely, that in the Bessemer vessel at the end of the blow, and before any addition has been made. This was mixed with small but gradually increasing quantities of silicon pig, and the product examined. The specimens have not yet been completely analysed, but they are arranged in order of silicon, beginning with a trace and ending with about 0·2 per cent. I hope shortly to publish full details (these have since been published *Journ. Chem. Soc.*, Feb., 1887). On comparing the hardness with tensile strength it will be seen that they vary together in a remarkable manner, the effect being entirely unlike that noticed in cast-iron. The fact that the material operated upon was a very near approach to homogeneous metal confirms the statement made in Part I. that in such material tenacity and hardness vary together. The results also appear to afford a proof of the correctness of the principle adopted in these experiments, as the values vary in different materials in a manner such as would be anticipated on theoretical grounds.

In Table E are given the results obtained in the case of four specimens of tyre steel, of which the analyses are given, but of which the tensile strength was not ascertained. It will be seen that they agree very nearly in chemical composition, and the hardness varies only from 21 to 24, which is about the ordinary limits for such material.

TABLE E.

*Tyre Steel—with Analyses.*

| No. | C. | Si. | Mn. | S. | P. | Hardness. |
|---|---|---|---|---|---|---|
| 1 | 0·58 | 0·23 | 0·64 | 0·03 | 0·03 | 24 |
| 2 | 0·59 | 0·40 | 0·63 | 0·04 | 0·07 | 23 |
| 3 | 0·52 | 0·23 | 0·61 | 0·01 | 0·06 | 21 |
| 4 | 0·62 | 0·15 | 0·57 | 0·01 | 0·04 | 22 |

I have also examined a number of specimens forwarded to me by Professor Kennedy, of University College, London. They were selected about three years ago for another purpose, for which, however, they were not employed. The results are given in Table F. The tensile strength and extension were measured by Professor Kennedy, and are given for comparison. The specimens varied in tenacity from about 29 to 46 tons per square inch, and include specimens ranging from the soft steel for boiler plates, up to the moderately hard metal used for tyres or rails.

It will be seen that the hardness is remarkably uniform throughout, and though there is a tendency for specimens with higher tensile strength to be slightly harder, still several exceptions will be found to this.

TABLE F.

*Steel Specimens from Professor Kennedy.*

| University College No. | Material. | Breaking load Tons per sq. in | Extension per cent On 2 ins. | Relative Hardness. |
|---|---|---|---|---|
| 4684 | Steel rail | 40·87 | 18·5 | 23 |
| 4914 | Steel Waggon Tyre | 42·30 | 25·0 | 24 |
| 4936 | Bessemer Steel | 42·56 | 20·0 | 21 |
| 4081 | Steel Fish Plate | 45 13 | 25·5 | 22 |
| 5013 | Steel Tyre | 45·94 | 20 5 | 22 |
| | | | On 3 inches. | |
| 5073 | Steel Tyre | 36·93 | 20·7 | 21 |
| 5077 | ,, | 37·13 | 24·7 | 23 |
| 5072 | ,, | 38·63 | 24·7 | 21 |
| 5071 | ,, | 40·70 | 17·3 | 21 |
| 5074 | ,, | 40·89 | 25·0 | 21 |
| 5078 | ,, | 41·17 | 23·7 | 21 |
| | | | On 7 inches. | |
| 1284 | Bessemer Steel Tyre | 31·31 | 22·9 | 21 |
| 1283 | ,, | 34·65 | 18·4 | 22 |
| 1298 | ,, | 35·79 | 16·1 | 21 |
| 1297 | ,, | 35·92 | 18·3 | 20 |
| 1256 | ,, | 36·14 | 18·1 | 22 |
| | | | On 10 inches. | |
| 2753 | Steel Boiler Plate | 29·09 | 22·7 | 21 |
| 2752 | ,, | 29·36 | 25·0 | 24 |
| 2751 | ,, | 29·53 | 24·0 | 21 |
| 2732 | ,, | 30·95 | 18·8 | 21 |

Allowance must of course be made for the probable experimental error of about ± 5 per cent.; but even then no direct connection between hardness and tenacity can be traced in this series of experiments. This would appear to point to the conclusion that in tyre steel, and similar material, we have not a homogeneous and structureless material, as in the case of nearly pure iron, but that the metal has more or less internal structure, possibly crystalline, which causes the hardness and tenacity not to vary together, as noticed in certain other cases.

TABLE G.

*Mr. J. T. Smith's Experiments on Steel Rails.*
*(Inst. C.E.*, xlii., p. 74.)

| No. | Strain required to punch a hole ⅞ in. diameter through web ¾ inch thick. | Tensile strength. Tons per sq. inch. | Carbon per cent. |
|---|---|---|---|
| 1 | 46·25 | 30·91 | 0·28 |
| 2 | 46 33 | 30·08 | 0·28 |
| 3 | 46·97 | 31·03 | 0·28 |
| 4 | 47·18 | 31·56 | 0 28 |
| 5 | 48·21 | 31·53 | 0·29 |
| 6 | 48 27 | 32·85 | 0·30 |
| 7 | 48·50 | 33·37 | 0·30 |
| 8 | 48·86 | 33·07 | 0·29 |
| 9 | 48·89 | 31·88 | 0·31 |
| 10 | 49·00 | 32 33 | 0 29 |
| 11 | 49 00 | 33·37 | 0·31 |
| 12 | 49·07 | 32·09 | 0·30 |
| 13 | 49·41 | 31·97 | 0·32 |
| 14 | 49 50 | 32·75 | 0·31 |
| 15 | 49·68 | 33 18 | 0·29 |
| 16 | 50·00 | 33·59 | 0·30 |
| 17 | 50·11 | 33·08 | 0·30 |
| 18 | 50·27 | 32 67 | 0·30 |
| 19 | 51·05 | 33·65 | 0·32 |
| 20 | 52·50 | 33·49 | 0·32 |
| 21 | 56·79 | 37·01 | 0·36 |
| 22 | 58·16 | 37·42 | 0·40 |
| 23 | 58·44 | 37 93 | 0·40 |
| 24 | 61·24 | 41·41 | 0·39 |
| 25 | 61·34 | 39·10 | 0 43 |
| 26 | 64·42 | 42·82 | 0·44 |
| 27 | 65·19 | 44·00 | 0·45 |
| 28 | 65·31 | 39·23 | 0 44 |
| 29 | 74·50 | 45·79 | 0 50 |
| 30 | 82·47 | 50·42 | 0·57 |

A very interesting series of experiments on the conditions affecting the wear of steel rails is recorded in a paper by Mr. J. T. Smith (*Inst. C.E.*, 1875, xlii., p. 69). Extracts from these results are given in Table G, from which it will be seen that "hardness" was measured by the force required to punch a hole ⅞ of an inch in diameter, through a web of metal ¾ of an inch in thickness. It will be seen from the table that the tensile strength increases very regularly as the proportion of carbon becomes greater, and that the "hardness" increases with equal regularity, and in the same manner. This appears to strongly support my contention, that the force required to make a measurable indentation will depend very greatly upon the tenacity of the material. It was found contrary to what was anticipated, that the "softest" rails generally wore best. This observation is supported by Dr. Dudley* and other writers of experience, though contested by some authorities. If the results of Mr. Smith's experiments are graphically represented (*Inst. C.E.*, xlii., p. 90), it is found that the curves of percentage of carbon, and the punching, tensile, and bending tests are of the same general form, and show a close agreement. The curve of percentage of wear, however, does not agree with these, but is quite irregular, and the differences observed in this respect are not so great as might have been expected from the other tests. It would appear from this that in the softer classes of steels, when not hardened by rapid cooling, the so-called "hardness," due to carbon, is really in a great measure due to tenacity, and that when correctly measured, the true hardness of this class of material does not usually vary over very wide limits. To me it appears probable that the best rails to wear would be those in which true hardness and tenacity are both high, while the material is not so altered as to render it too sensitive to sudden shock. Internal structure doubtless also has a most important influence.

Mr. Smith's experiments appear to conclusively prove the unreliability of the method of indentation as a measure of hardness, while his observations on the wear of this class of material fully support the results given in Table F, in which it is shown that the hardness varies within narrow limits, and does not differ much from that of good wrought-iron, or of soft cast-iron of good quality.

From these observations I am inclined to suggest the following values as results which may be anticipated from an apparatus like my own, used in the manner described:—

| Material. | Hardness. |
|---|---|
| Extra pure iron, tensile strength, 22 tons .. | 17 |
| Soft and weak cast-iron .. .. .. .. .. | 18 |
| Mild steel, tensile strength, 30 tons .. .. | 21 |
| Tyre steel ,, ,, 40 ,, .. .. .. | 21—24 |
| Cast-iron, maximum tensile strength .. .. | 21—24 |
| Iron for rolls about.. .. .. .. | 30 |
| Hard scrap about.. .. .. .. | 40 |
| Very hard white iron about.. .. .. .. | 70 |

Here the matter must be left for the present, but at a future time I hope to pursue these investigations further.

## THE AMSTERDAM EXHIBITION OF FOOD AND COOKERY.

GREAT preparations are being made in Amsterdam for the Exhibition of articles of food and cookery, which is to be opened in that city in June next. Much interest in the Exhibition has been excited not only in Holland, but in Germany, Belgium, and France. A number of exhibitors are coming from England. The object of the Exhibition is to extend the knowledge of the various vegetable and animal kinds of nourishment provided by nature for the benefit of man; to furnish by mutual comparison a stimulus to further improvement, both in the cultivation and preparation of these articles; and at the same time

* Compare Snelus. *Jour. Iron and Steel Inst.*, 1882, ii., pp. 585, 596.

to disprove in the most convincing way the prejudices which too often prevent or hamper the general introduction of useful means of nourishment. A feature of the Exhibition, which partakes of a philanthropic character, is the fact that the promoters are not pecuniarily interested in the concern. Their idea is the introduction into Holland of articles which other countries manufacture, and the Dutch people might use. It is believed that there is a large market for English goods yet to be opened in Holland. The reason why there is at the moment so limited a hold on the Dutch market, is that almost all goods imported reach the retailer through the hands of middlemen. There is little doubt that English wares are not of themselves too dear for Holland. With a view to encouraging the presence of British exhibits, not only has the cost of space been reduced, but the railway and steamer rates have been greatly lowered. It has also been provided that no Customs' duties shall be charged. Other considerable facilities are announced in addition. Part of the Exhibition grounds will be fitted up as a seventeenth century town-hall market-place, fish-market, &c., and a large square will be set apart for concerts and entertainments of a varied character. In the evening there will be fireworks as at our own Inventions Exhibition. The Exhibition will remain open from June till September. The classes of exhibits range under eight chief groups,—animals and plants, living or fresh, supplying articles of food; articles of food in raw or partially prepared condition; articles of food ready for use; malt liquors, mineral and aërated waters, fruit juices, lemonades, &c.; appliances used in the manufacture, preservation, and transport of the articles; appliances for analysing and testing articles of food, beverages, &c.; articles of food prepared in the kitchen for immediate use; dining rooms (penny dinners), modes of serving up food, crockery, table linen, lamps, cutlery, &c., &c. A separate catalogue is devoted to the exhibits coming under the head of agriculture and horticulture. There will be a series of competitions, for which gold medals and prizes of five hundred francs are to be given; also a series of exhaustive lectures on cookery. Applications for space are to be sent in immediately.

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

*Ordinary Meeting, May 5th, 1887.*

Mr. William Crookes, F.R.S., President, in the Chair.

Messrs. T. Cooksey, George Robertson, David Wilson, Jun., and George Collar were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Hugh Barclay, Rose Hill, Harrington, Cumberland; John Edward Green, 68, Portland Road, Holland Park, W.; William Marshall, 7, Walter Street, Nottingham; Frederick Lawrence Overend, B.A., Blair Lodge School, Polmont, N.B.; J. Stanley Phillips, Wentworth, Upper Long Ditton, Surrey; Walter Shelley Spencer, 142, Clifton Street, Brooks Bar, Manchester; Charles Ernest Stedman, Williamstown, Melbourne.

The following papers were read:—

41. "*A Contribution to the Study of Well Water.*" By R. Warington, F.R.S.

The proportion of chlorine in the rain water at Rothamsted is 2 per million; the proportion of total combined nitrogen about 0·7 per million.

Of 31 inches of rain, annually falling on a bare clay soil, 17 inches have evaporated and 14 inches percolated below 5 feet. Drainage chiefly occurs between October and February. The quantity of chlorine in the drainage from 5 feet of soil is the same as that in the rain, but the proportion is doubled in consequence of evaporation. The proportion of nitrogen as nitrates in the drainage water from 5 feet of bare clay soil has averaged 10·7 per million. The production of nitrates in the soil is chiefly during summer; the principal discharge of nitrates as drainage is in the autumn.

When land is covered with vegetation evaporation is increased, and the winter drainage commences at a later period. Evaporation being increased, the chlorine in the drainage water may also be increased. The drainage from the Rothamsted unmanured wheat land contains 6 per million of chlorine; the drainage from the plot manured with farmyard manure, 7·3 per million. While vegetation is active no nitrates are found in the drainage water from the unmanured wheat; the nitrates reappear in autumn, after harvest. The average proportion of nitrogen as nitrates in the drainage from unmanured wheat is 3·4 per million; from wheat receiving farmyard manure, 5·8 per million. These are minimum numbers. With rain containing the amount of chlorine found at Rothamsted, the average proportion of chlorine in drainage water can hardly exceed 8 per million.

The pure well waters of Harpenden contain a minimum of 4·4 of nitric nitrogen per million; this, therefore, is the average amount in the drainage water of the district.

The deep wells in the chalk of Harpenden derive their main supply from a flow of underground water proceeding from north-west to south-east. Each well has besides its own local drainage. The pure well waters contain about 11 per million of chlorine; this amount does not sensibly vary throughout the year. Wells contaminated by sewage are generally at their maximum purity in October. They may show a commencement of a rise in chlorides one or two months after active autumn drainage has commenced. All through the drainage season, the effect of one month's drainage is not manifested in the well water till the following month. The maximum of chlorides in the contaminated wells occurs after the end of the drainage season—usually in March. The nitrates and chlorides increase at a nearly equal rate during the early months of the drainage season. If active drainage continues for three months, a great increase in the proportion of nitrates will usually then take place, and this relative excess of nitrates is maintained for some months. The proportion of nitrates to chlorides varies considerably in different contaminated wells. The sewage for poorly fed population yields a high proportion of chlorides to nitrates. Stable sewage furnishes apparently a high proportion of nitrates to chlorides. The old sewage contamination of deep wells is generally more or less chloric, chlorides being more permanent than nitrates.

The well waters of Harpenden contain the nitrifying organism in small proportion; it is probably derived from surface soil which has fallen in.

In the contaminated waters the quantity of silica is not increased, and the quantity of carbonates but little increased. Lime is considerably increased, and magnesia still more. Nitrates, chlorides, and sulphates are largely increased.

On comparing the low proportion of chlorine found in the pure chalk waters of Harpenden, near the edge of the London basin, with the amount found in other chalk waters, and especially with the chalk waters beneath the London clay,—and considering further the proportion of chlorides which can possibly be contributed by rain,—it appears highly probable that a portion of the chlorides in chalk water, and probably in the water of other strata, is derived from a residue of sea-salt remaining in the rock.

The proportion of nitrates found in the waters of uncontaminated wells and springs in the permeable strata of England is fairly constant; it indicates an average loss to the soil of about 7 lbs. of nitrogen per acre per annum.

42. "*Crystals in Basic-Converter Slag.*" By J. E. Stead and C. H. Ridsdale.

The authors describe a variety of crystals found near the centre of blocks of basic-converter slag, weighing 40 to 50 cwts. each, which had cooled slowly.

No. 1. Large, well-formed, flat square crystals, of a faint yellowish colour, consisting essentially of the phosphate $4CaO \cdot P_2O_5$; these have also been described by Hilgenstock.

No. 2. Blue crystals, previously noticed by Gioddeck and Brockmann; these appear to be a double calcium silicate and phosphate, $CaO \cdot P_2O_5, CaO \cdot SiO_2$. Vanadium protoxide was present to the extent of 1·64 per cent.

No. 3. Feathery or fern-like crystals; these are remarkable, as they contain under 4 per cent of acid oxides and over 95 per cent of basic oxides—chiefly of calcium, magnesium, iron (protoxide and peroxide), and manganese.

No. 4. Hexagonal, needle-shaped, lemon-coloured crystals, which appear to consist of about 86 per cent $4CaO \cdot P_2O_5$ with 10 to 11 per cent of silicates of metallic oxides.

Nos. 5 and 6. Two varieties of flat black needles, the one magnetic, the other not. No. 5 contained about 10 per cent $CaO \cdot Al_2O_3$, 45 per cent $3CaO \cdot Fe_3O_4$, and 33·5 per cent $3CaO \cdot Fe_2O_3$. No. 6 contained about 15 per cent $CaO.Al_2O_3$ and 73 per cent $3CaO \cdot Fe_2O_3$.

Discussion.

In reply to a question by Mr. Thompson, Mr. Ridsdale stated that Mr. Meiers had determined the crystalline forms of the substances which had been described, and had examined them in polarised light. In reply to Mr. Nettlefold, he said that they were of opinion that the whole of the phosphorus was present as $4CaO \cdot P_2O_5$.

43. "*Note on the Influence of Temperature on the Heat of Dissolution of Salts in Water.*" By William A. Tilden, D.Sc., F.R.S.

In a paper which appears under this title in the April number of the *Transactions*, Mr. Pickering reviews the experiments which he had previously published upon the same subject, and so far modifies the conclusions which he had drawn from those experiments as to admit that the lines representing the heat of dissolution of various salts at successive temperatures do not consist of a series of curves following one another at irregular intervals. But Mr. Pickering maintains that the new experiments now published lead to a result which only differs in degree from his former conclusion, and involves admissions which are essentially of the same character as those which he has abandoned. His main conclusion will be best expressed in his own words (p. 335):—"The heat of dissolution of a salt increases uniformly with the temperature up to a certain point, when the rate of increase is suddenly lowered, and this fresh rate continues uniform till lowered again at some higher temperature," &c.

The consequence of this is that the graphic representation of the results must, according to the author, consist of two or more straight lines, which in the cases which he has examined, and within the limits of temperature to which his experiments have been confined, meet at 8° to 10°, or in some cases at higher temperatures. And although the suggestion was made by Dr. Alder Wright, at the discussion which followed the reading of the paper, that the results might be represented by continuous curves without these breaks, the author deliberately rejects this suggestion, and adds a postscript to his paper emphasizing his own view.

The experimental work upon which this conclusion is based is, if not quite unimpeachable, at any rate of a high order of excellence, surpassing any other published work on the same subject within my knowledge. It is only in the interpretation of the results that I venture to differ from Mr. Pickering, but I think it is so plain that his main proposition is untenable, that I feel it desirable to direct attention to the question whilst the work is fresh in the recollection of the Society.

Without any desire to be hypercritical, I think some exception might be taken to the way in which the means appear to have been arrived at. Instead of taking the arithmetical means of the values resulting from experiments performed at the several temperatures, the mean results have been deduced from the lines representing the various series, whether experiments were done at all the points or not (p. 304). The effect of this is naturally to straighten on the line between temperatures where experiments were not made.

I may also remark that in the statement of the differences (postscript, p. 336) between the values calculated from the equation for the curve and the author's values, the word "observed" values must be understood as these "mean" observed values which are not the exact mean values for each temperature. But after all this way of calculating affects the values of the mean to a very small extent, and has not destroyed their significance. Taking Mr. Pickering's own figures as representing the mean experimental results at the successive temperatures, and simply plotting them out on squared paper, I submit that inspection is sufficient to show that every one of his series conforms to a continuous curve, which, considering the difficulties of the work, is generally quite remarkably smooth and free from irregularities.

With reference to potassium chloride, the author remarks (p. 304) that "the sixteen mean results from 10—25° inclusive evidently form a straight line," and that the experiments below 9° form another straight line. To this I demur. I do not see how such an idea could have arisen, unless it was from the differences tabulated on p. 306, from which it appears that the increase in the value of M per degree drops from 50 cals. between 8° and 9° to 42 cals. between 9° and 10°. Looking at other parts of the table, however, it will be noticed that even greater irregularities occur, as for instance—

| | | |
|---|---|---|
| at 16—17° | the difference is | 33 cals. |
| 17—18 | ,, | 45 ,, |
| 18—19 | ,, | 36 ,, |

If a fall of 8 cals. at 8° to 9° is held to justify the assumption of a break in the line at this point, why should not another break be accepted when there is a rise of 12 cals. or a fall of 9 cals. in the rate at the temperatures referred to?

Similar remarks apply in other cases. Potassium nitrate, for example, shows a change in the rate of increase

from 40 cals. at 12—13°
to 23 ,, 13—14.

It is not clear why the break should be introduced here, when at only one degree higher there is a change of greater amount, viz.—

from 23 cals. at 13—14°
to 42 ,, 14—15,

and yet no corresponding change is recognised in the curve.

In discussing these curves I have added the graphic representation of all the experiments, in order that they may be compared with the means, and that no injustice may be done to the author's view.

Again, in the case of sodium chloride the mean differences given in the Table (p. 308) seem to indicate, if any, four rather than two straight lines, the value being—

| | |
|---|---|
| 3— 7° | 44·5 cals. |
| 7—11 | 38·0 ,, |
| 11—18 | 31·7 ,, |
| 18—25 | 29·5 ,, |

Though the curves are somewhat irregular in some of the other cases, especially that of sodium carbonate, the hypothesis of sudden breaks is not supported sufficiently to make it acceptable in the face of all the probabilities pointing the other way. Such irregularities might

naturally be expected in work of this nature, surrounded with difficulties as it is.

Mr. Pickering criticises severely the results I obtained in the attempt to get determinations of the heat of dissolution over a considerable range of temperature. I am indebted to Mr. Pickering for reminding me of the necessary validity of the formula of Person, which shows the dependence of thermochemical effects upon temperature. The discrepancy between the calculated values in that paper and the experimental results arose from the mistake of assuming the values for the specific heats of the several solutions to be practically constant throughout, whereas they increase with rise of temperature, though to an extent which, according to the experiments of Marignac, is very small, from about 20° C. to 50°. But this does not destroy the experimental numbers which, though subject to a general error which makes them all somewhat too low, are consistent among themselves, and support the conclusion that the rate at which the heat of dissolution is influenced by temperature diminishes as the temperature rises. Fortunately this accords with the results of Mr. Pickering's own work, whether we do or do not adopt the hypothesis which he prefers, that the changes occur suddenly. In my opinion all the probabilites, in addition to Mr. Pickering's own results, indicate that the heat of dissolution of a salt in water is a continuous function of the temperature.

### Discussion.

Mr. Pickering, in reply, said that, after a very careful re-examination of his results, he found it impossible to accept Prof. Tilden's interpretation of them. In the first place he defended the method which he had employed in deducing mean values: this consisted in separately plotting each series of experiments by drawing lines to connect the various values of each series, and deducing the final mean by taking the mean of the values given by these lines at each degree; and it was to be noted that the means were not deduced from the lines representing the individual series after the irregularities in them had been smoothed out, as in the dotted lines in Plate I., as Prof. Tilden appeared to think they were,—probably through a want of clearness in the explanation given at p. 304 of the speaker's paper. The method described would give unfair results in the event of one series containing a far larger number of determinations than another, and to avoid this he had never applied the method when a greater interval than 2° separated the successive experiments in any series. Though not perfect, this method is certainly the fairest which can be adopted, and beyond comparison much fairer than that suggested by Prof. Tilden. Two series, consisting of experiments performed at alternate degrees and free from any experimental error, except that made in standardising the thermometers (which would cause the results of one series to be uniformly above, and those of the other uniformly below the truth), would each yield a straight line, if such were the nature of the true results, whereas their mean deduced by Prof. Tilden's method would be a wavy line, and was obviously incorrect.

Mr. Pickering said that the concordance between his results and the curve or straight line method of representing them was so close that it was quite impossible by mere inspection of a diagram to decide which method was the best. The whole question depended on the magnitude of the average error in the two cases, and Prof. Tilden had brought forward no numbers to show that a curve indicated a smaller error than straight lines. On the other hand, Mr. Pickering had examined the average error in the two cases very carefully. In the additional note to his paper he had shown that a curve (deduced from the actual results just as the straight lines were deduced from the actual results) did not agree with the mean results so well as his straight lines: in the six cases which he examined the curve would represent a very considerable increase in the average error, and at the same time the sign of the error in the individual experiments was not positive and negative promiscuously as in the straight line diagram, but errors of like sign were grouped together, the numbers deduced from the curve being above the actual results throughout a considerable range, and then below them throughout another considerable range.

Mr. Pickering had examined in the same way the results of each individual series performed with potassium chloride; the average errors, according to the two methods of representing the results, were—

| | Straight line. | Curve. |
|---|---|---|
| '08 A .. .. | 4·7 cals. | 5·3 cals. |
| '61 A .. .. | 4·0 ,, | 5·7 ,, |
| '08 B .. .. | 1·3 ,, | 4·7 ,, |
| '61 B .. .. | 4·6 ,, | — |

Thus in every case the curve did not represent the results so closely as the straight line. With series '61 B the "curve" equation obtained represented a practically straight line.

Another way in which he had attempted to investigate the question was to find the equation which represented those portions of the diagram which he considered straight (from 9° to 25° with potassium chloride), and to see whether they gave a curve which could by any means represent the other results (below 9°). The various values of $\beta$ in the equation to the curve $(1+\alpha t+\beta t^2)$ which he obtained were—

| | | | |
|---|---|---|---|
| Mean of 9 equations from series | | '08 A | +0·094 |
| ,, 8 ,, | ,, | '61 A | −0·056 |
| ,, 2 ,, | ,, | '08 A | +0·094 |
| ,, 2 ,, | ,, | '61 A | +0·674 |
| Mean (weighted according to number of experiments included) .. .. | | | +0·025 |

which value represents a line so nearly straight that it would deviate from straightness by only 4 cals. from 9° to 25°, or 6 cals. from 3° to 25°, whereas the actual results show a deviation of 152 cals. between these last-mentioned limits. The results from 9° to 25° are, therefore, not conformable with those from 9° to 3°. Thus in every way in which the results are examined they undoubtedly favour the straight line as opposed to the curve method of representation.

In answer to Prof. Tilden's question referring to the results given in Table I., Mr. Pickering said that he thought it obvious why he should have taken the increase of 42 to 50 cals. (9° to 8°) as significant of a true alteration in the rate, and should not have taken the diminution of 45 to 33 cals. (18° to 17°) as having any significance at all: in the latter case the difference of 45 cals. is evidently an exceptionally high result, unsupported by any other observation, which when combined with the differences immediately preceding and following it (36 and 33 cals.) gives the same mean as 16 differences from 25° to 9°, whereas the difference of 50 cals., while higher than any differences preceding it, is identical with the mean of the five differences which succeed it (8° to 3°).

He thought that no theoretical speculation should induce us to reject the more correct method of representing his results in favour of the less correct method. Finally, he pointed out that, although the influence of temperature on any chemical change is represented by a curve, this curve really occupies but a very small proportion of a diagram representing the effect of temperature from the absolute zero to the highest known temperatures, and that this diagram consists of practically straight lines inclined to each other at different angles, and joined by curves, presenting an appearance, when reduced to the same scale, precisely analogous to that which he considered his dissolution results presented.

44. "*The Distribution of Lead in the Brains of Two Factory Operatives Dying Suddenly.* By A. Wynter Blyth.

At a certain lead factory in the East of London five cases of more or less sudden death at different dates have been attributed to the effects of lead. In two of the cases the author had an opportunity of making a toxicological investigation. In the one case 24·25 m.grms. of lead sulphate was separated from the liver and 5·4 m.grms. from one kidney; there was also lead in the brain.

In the second case investigated, occurring about a year after the first, the brain was more exhaustively examined, the cerebrum and cerebellum being treated separately and divided up by suitable means into white matter, kephalin, ether extract, substances soluble in cold alcohol and albumenoid residue, and the lead determined in each.

| | Cerebrum, 460·8 grms. | Cerebellum, 156·2 grms. |
|---|---|---|
| Aqueous extract | 1·1 m.grms. | 0·4 $PbSO_4$ |
| White matter (kephalin-free) | — | 5· ,, |
| Kephalin | 1·5 ,, | 6·0 ,, |
| Ether extract (from which kephalin had been precipitated) | — | — |
| Substances soluble in cold alcohol | — | — |
| Albumenoid residue | 40·0 ,, | 6·0 ,, |
| | 42·6 | 17·4 |

Calculated on the whole cerebrum this would amount to 99·7 m.grms., or a possible total for the whole brain of 117·1 m.grms. $PbSO_4$.

There has hitherto been no reasonable hypothesis to explain the profound nervous effects of the assimilation of minute quantities of lead; but if it is allowed that lead forms definite compounds with essential portions of the nervous system, it may then be assumed that in effect it withdraws such portions from the body; in other words, the symptoms are produced not by poisoning in the ordinary sense of the term, but rather by destruction,—a destruction it may be of important nerve-centres.

45. "*Researches on Silicon Compounds and their Derivatives.* II. *A New Chlorobromide of Silicon.*" By J. Emerson Reynolds, M.D., F.R.S.

In purifying a large quantity of silicon tetrabromide prepared by means of crude bromine, the author has separated a portion boiling at 140° to 141°, of the relative density 2·432, which analysis shows to be the chlorobromide of the formula $SiBr_3Cl$.

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At the next meeting, on May 19th, there will be a ballot for the election of Fellows, and the following papers will be read:—

"The Formation of Hyponitrates." By Prof. Dunstan and T. S. Dymond.

"Ozone from Pure Oxygen; its Production and its Action on Mercury, with a Note on the Silent Discharge of Electricity." By W. A. Shenstone and J. T. Cundall.

"The Thermal Results of Neutralisation and their Bearing on the Nature of Solution and the Theory of Residual Valency." By S. U. Pickering.

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## ROYAL INSTITUTION OF GREAT BRITAIN.

*Annual Meeting, May 2, 1887.*

Sir William Bowman, Bart., LL.D., F.R.S., Manager and Vice-President, in the Chair.

The Annual report of the Committee of Visitors for the year 1886, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The real and funded property now amounts to above £83,000, entirely derived from the contributions and donations of the members.

Forty-eight new Members paid their admission fees in 1886.

Sixty-three lectures and nineteen evening discourses were delivered in 1886.

The Books and Pamphlets presented in 1886 amounted to about 288 volumes, making, with 443 volumes (including periodicals bound) purchased by the Managers, a total of 731 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as officers for the ensuing year:—

*President*—The Duke of Northumberland, K.G., D.C.L., LL.D.

*Treasurer*—Henry Pollock.

*Secretary*—Sir Frederick Bramwell, D.C.L., F.R.S., M. Inst. C.E.

*Managers*—Joseph Brown, Q.C.; Sir James Crichton Browne, M.D., LL.D., F.R.S.; The Earl of Crawford and Balcarres, F.R.S., F.R.A.S.; Frank Crisp, LL.B., B.A., F.L.S.; Warren de la Rue, M.A., D.C.L., F.R.S.; Henry Doulton; John Hall Gladstone, Ph.D, F.R.S.; Sir William Withey Gull, Bart., M.D., D.C.L., F.R.S.; William Huggins, D.C.L., LL.D., F.R.S.; Alfred Bray Kempe, M.A., F.R.S.; George Matthey, F.R.S., Assoc. Inst. C.E.; The Right Hon. Earl Percy; Sir Frederick Pollock, Bart., M.A.; William Henry Preece, F.R.S., M. Inst. C.E.; Edward Woods, Pres. Inst. C.E.

*Visitors*—Forster F. Arbuthnot; Shelford Bidwell, M.A., F.R.S.; John Birkett, F.L.S., F.R.C.S.; Michael Carteighe, F.C.S.; The Very Rev. Dean Church, M.A.; Edwin Cutler; James Farmer; Charles Hawksley, M. Inst. C.E.; David Edward Hughes, F.R.S.; John W. Miers; Frederick Purdy, F.S.S.; Lachlan Mackintosh Rate, M.A.; William Chandler Roberts-Austen, F.R.S.; George John Romanes, M.A., LL.D., F.R.S.; James Wimshurt.

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## CORRESPONDENCE.

### THE INSTITUTE OF CHEMISTRY.

Sir,—The secrecy with which the Institute carries on its existence is, I imagine, unparalleled, except among avowedly secret societies. Writing to the secretary some months ago for particulars as to terms of admission, I was vouchsafed no reply. I have, however, been informed by one F.I.C. of the following particulars:—

1. That the annual subscription has been reduced to half-price, *i.e.*, to one guinea.
2. That candidates are now admitted *without examination.*
3. That the Council propose to obtain, if they can, an Act of Parliament excluding from the profession all who are not Fellows of the Institute.

Possibly, the publication of this may induce the chemical sphinx to reveal.—I am, &c.,

F.C.S.

May 7, 1887.

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**Influence of Pressure in the Modification of Dissolved Chlorides.**—G. Foussereau.—The electric resistance of a solution of ferric chloride containing 1·33,260th of that salt diminished from 114,310 to 113,160 after ninety minutes of a pressure of 175 atmospheres. The resistance has, therefore, declined by about one-hundredth of its value, showing that the modification of the chloride by water has increased under the influence of pressure, since this alteration is accompanied by an abatement of resistance.—*Comptes Rendus*, civ., No. 17.

## NOTICES OF BOOKS.

*Report on the Waters of the Hudson River, together with an Analysis of the same.* By C. F. Chandler, Ph.D. New York: Trow's Printing and Bookbinding Co. 1885.

The examination of the water of the Hudson River was made with special reference to its present condition, and to whether it is still safe to rely upon it as a source of supply for the city of Albany. The water was examined for a similar reason in 1872, and was found to be of satisfactory quality; but as many changes have occurred since that time it was thought advisable to have fresh tests made, especially with regard to sewage contamination. This was effected by distilling the water with permanganate of potash, and carefully estimating the ammonia formed. The samples were taken from the river at the inlet to the pumping-station. The results are given in tabular form. Table II. gives them in grains per United States gallon of 231 cubic inches, and Table III. shows them as parts per 100,000. For the purpose of comparison tables of analysis of other American and foreign waters are also given.

Careful examination of these results shows that the water at Albany contains a smaller quantity of albumenoids than the water above Troy (which is higher up the river), in spite of the fact that there is undoubtedly some contamination in its passage past Troy. This is entirely in keeping with the theory of spontaneous purification about which so much has been written and said by Drs. Tidy, Frankland, Warington, and others; but there are still some chemists who do not believe in this theory. Mr. Chandler inserts a few quotations from well-known writers on the subject.

A further comparison of the Hudson River water at Albany with the chief waters used in America and England shows that the Hudson water does not contain any excessive quantity of organic matter.

Great stress is now laid by many persons on what is called the biological analysis of water,—that is, the study of the minute organisms which for more than two hundred years have been known to exist in water. Fermentation, which was first supposed to be a purely chemical action, is now ascertained to be entirely due to the agency of these organisms. This and other discoveries gave rise to what is known as the "germ theory" of disease—that many diseases were due to the presence of peculiar micro-organisms.

As an example of the popular idea of germs we may mention a case which has recently occurred within our knowledge: a well-known chemist received a sample of water, and a note requesting him to examine it for scarlet fever, and state how much there was in it. If these bacteria, &c., were only present in bad or polluted water, there would be some grounds for such an assumption, but as a matter of fact they are omnipresent; it is almost impossible to get a drop of water which does not contain them. Under these circumstances, says Dr. Chandler, it would appear that counting the number of bacteria that will develop in gelatin on the addition of a sample of water is not a very reliable method for determining the quality of water for domestic purposes.

After examining the water of the Hudson River by every possible method, Mr. Chandler finds no evidence which could lead him to change the opinion expressed in 1872, and there is no reason why the city of Albany should not continue to use this water.

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**Sale of Food and Drugs Act.**— Mr. Bernard Dyer, B.Sc., F.C.S., has been appointed Public Analyst for the City of Truro.

**Artificial Production of Magnetite.**—Alex. Gorgen. —The author has reproduced this mineral by a novel process, consisting essentially in the action of iron sulphide upon an alkaline sulphate.—*Comptes Rendus*, civ., No. 17.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 17, April 25, 1887.

**Rapid Determination of Active Limestone in Soils.** —Paul de Mondésir.—When a vessel is partly filled with water saturated with carbonic acid, this gas diffuses itself slowly in the air, which fills up the remaining space in the flask. After agitation for about a minute an equilibrium of distribution of the carbonic acid between the air and the water is reached provided that the water occupies only a small portion of the flask. Upon this fact the author founds an apparatus and a process for the rapid approximate determination of the available calcareous matter in soils. The apparatus cannot be intelligibly described without the accompanying figure.

**Method of Detecting Correlations between Two Orders of Facts.**—M. de Montessus.—The author calls attention to the dangers of this method. It consists essentially in taking two chronological series of natural facts, between which a relation has been supposed, *à priori*, and in searching for their coincidences. But as far as it is known to him the following problem has not been analytically solved, there being given two series of points arranged upon two right lines according to laws which are known in the one case and which are to be found in the other, what will be for a hundred points the minimum number of coincidences allowing us to believe in a correlation of cause and effect between the two orders of phenomena?

**On the Alkaline Vanadates.**— A. Ditte.—The author has examined and described six lithium vanadates. The anhydrous salts of all the alkaline metals are reducible to a small number of simple formulæ; the hydrates contain proportions of water which vary with the circumstances of crystallisation, but their general properties are the same. The acid salts are of a red colour, more or less inclining to orange; the neutral salts are colourless, and the basic salts are some of them coloured and some colourless.

**The Hydrates of Sodium Arseniate.**—H. Lescœur. —The author finds the water in the crystalline sodium arseniates differs in quantity from 43 to 57 per cent.

**Qualitative Detection of the Suphites in presence of Hyposulphites and Sulphates.**—A. Villiers.—This paper will be inserted in full.

**On the Sulphurous and Degenerated Sulphurous Waters of Olette.**—Ed. Willm.—This paper, though placed under the head "Analytical Chemistry," does not contain any novel or improved analytical method.

**On Synthetic Aceto-nitrile.**— Louis Henry.—The acetonitrile obtained by the author's process is perfectly identical with that obtained by the dehydration of acetamide.

**The Presence of Normal Butylic Alcohol in a Brandy from Cognac; Comparison of the Higher Alcohols of this Brandy with those Produced in the Fermentation of Sugar by Elliptical Yeast.**—E. Claudon and E. C. Morin.—In this brandy normal butylic alcohol and butyric acid are present. The brandy in question was not saleable on account of its strong savour of butyric acid, which was present to the extent of 117·4 grms. per hectolitre of absolute alcohol. The brandy contained 48·1 propylic alcohol, 18·5 isobutylic alcohol, and 139·5 grms. amylic alcohol as against 3·1, 2·4, and 80 grms. of these products found in the alcohol obtained from the fermentation of sugar by the elliptic yeast.

**On Bichlorated Ethylic Alcohol.**—Maurice de Lacre.—This compound is a colourless liquid, thick and viscid, of a characteristic odour and of an aromatic and pungent flavour. It does not solidify in a freezing-mixture of sodium sulphate and hydrochloric acid. Its specific gravity at 15° is 1·145. It boils without decomposition at 146°. Its vapour density is 3·93 experimentally, or 3·97 theoretically. It is sparingly soluble in water, but dissolves readily in alcohol and ether. It reduces ammoniacal silver nitrate, and does not dissolve calcium chloride.

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*Journal de Pharmacie et de Chimie.*
Series v., Vol. xv., No 5, March 1, 1887.

**Metals and Minerals from Ancient Chaldea. Sources of Tin in Antiquity.**—M. Berthelot.—Already noticed from the *Comptes Rendus*.

**Disinfection Stoves.**—From the experiments here described it is concluded that the moist steam stove at high pressure, as proposed by MM. Geneste and Herscher, is an excellent instrument for disinfection. At the temperature of 106° all the pathogenic microbia tried were found to have been killed, even in a mattress. Dry air and steam without pressure were found much less efficacious.

**Behaviour of Different Bacteria in Potable Water.**—Meade Bolton.—Water not containing sufficient organic matter to be detected by our analytical methods is capable of nourishing the lower micro-organisms, and of permitting their multiplication.

No. 6, March 15, 1887.

**Certain Coloured Reactions of the Arsenic, Vanadic, Molybdic, and Arsenious Acids.**—M. Lévy.—Already noticed.

**New Ureometer.**—Dr. Georges Frütiger.—This illustrated paper is from the *Bulletin de la Soc. Chimique*.

**Action of Mercurial Vapours upon Leaves.**—Victor Jodin.—The author has observed that the activity of the respiratory function becomes greater when the leaf is exposed to the influence of mercury. A second fact, quite unforeseen, is that leaves exposed to mercury lose their power of resistance to desiccation. A litre of air saturated with mercurial vapour at 20° contains at most 0·00071 grm. of mercury, and yet this quantity is sufficient to mercurialise 30 grms. of fresh leaves.

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*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* 4th Série, Vol. ii., March, 1887.

**New Production of the Alkaline Metals.**—H. X. Castner.—This process consists in reducing the alkaline hydroxide or carbonate, when melted, at a moderate temperature, by causing a metallic carbide or its equivalent to react upon it, thus dispensing with the large quantity of carbon, and with the lime now employed. The reducing agent employed remains below the surface of the alkaline bath, and is consequently kept in constant and direct contact with the melted alkali. It is formed by coking an intimate mixture of tar and iron, the latter in a fine state of division, as obtained by the action of hydrogen. For each kilo. of pure caustic soda there are required 22 kilos. of this iron carbide. The operation is effected in large cast-iron crucibles. The yield may reach 90 per cent.

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*Archives Neerlanaaises des Sciences Exactes et Naturelles.*
Vol. xxi., Part 4.

This issue contains no chemical matter.

*Bulletin de la Société Chimique de Paris.*
Vol. xlvii., No. 3, February 5, 1887.

**Artificial Production of Zincite and Willemite.**—Alex. Gorgen.—The author has obtained zincite, crystalline zinc oxide (which had previously been formed artificially by several chemists), from zinc sulphate, nitrate, and fluoride. Willemite, a natural neutral zinc silicate, has also been previously obtained artificially. The author forms it by the action of silica upon several salts of zinc.

**Relations of the Efflorescence and the Deliquescence of Salts with the Maximum Tension of Saturated Solutions.**—H. Lescœur.—The author gives two tables, the one containing the maximum tension at +20° of certain saturated solutions, represents the scale of deliquescence at this temperature. The second, which gives the dissociation-tensions of various hydrates at +20°, representing the scale of efflorescence at this temperature.

**Maximum Tensions of the Vapour of Sodium Acetate.**—H. Lescœur.—The author prepares three systems of solutions of this salt and determines their vapour tensions, which are given in the form of tables.

**Neutralisation-Heats of the Malic and Citric Acids and their Pyro-derivatives.**—H. Gal and E. Werner.—It appears that the total neutralisation-heat of the pyro-acids (excepting the itaconic) is higher than that of the generating acids by about two calories. This is a relation analogous to that already observed between the monobasic acids and the corresponding alcohol-acids.

**Neutralisation-Heat of Meconic and Mellic Acids.**—H. Gal and E. Werner.—The numbers yielded by meconic acid are lower than the corresponding ones of mellic acid. The heat liberated in neutralisation diminishes in proportion as this advances. In the first place are observed values corresponding to the most energetic acids, then to the alcohol acids, and lastly to the weak acids. The figures obtained for mellic acid enable us to foresee some well-known facts. Neutral sodium mellate, if evaporated with an excess of hydrochloric acid, loses a part of its base, and gives an acid salt. This same salt is produced on heating an alkaline chloride with mellic acid. These numbers lead us to think of the polybasic mineral acids in which the different hydroxyls are fixed on the same radicle, and which yield similar thermic results, such as the sulphuric, chromic, and phosphoric acids.

**Neutralisation-Heat of the Glyceric and Camphoric Acids.**—H. Gal and E. Werner.—These figures confirm entirely the remarks made in a former communication.

**Caprylic Aldoxime and Methl-hexylic Acetoxime.**—A. Béhal.—These two bodies have a similar appearance, but differ in their boiling-points; aldoxime boils at 121° to 123°, and acetoxime at 116° to 117°. Both are oily liquids, which stain paper. Their odour is aromatic, mixed with something fetid, and is very tenacious. They do not solidify if exposed for an hour to a mixture of ice and salt. They are lighter than water, and dissolve readily in alcohol and ether.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

**Watermark in Paper.**—We shall be glad to supply information respecting imitation watermarks on application.—Cross and Bevan, 4, New Court, Lincoln's Inn, W.C.

**Action of Mercury on Steel.**—Could any of your readers kindly inform us what action quicksilver has on steel by constant immersion; whether it coats it or perforates it in time? If so, could they tell us what metal quicksilver has no effect upon?—F. & S. Dixon.

[Mercury has no solvent action on steel or iron; it merely wets the surface and adheres to it, in the same way that water wets glass.—Ed. C.N.]

## MEETINGS FOR THE WEEK.

MONDAY, 16th.—Society of Arts, 8. (Cantor Lectures). "The Chemistry of Substances taking part in Putrefaction and Antisepsis," by J. M. Thomson, F.C.S.
—— Society of Chemical Industry, 8. "Note on the Action of Zinc Chloride on Castor Oil." by Dr. C. R. A. Wright, F.R.S. "New Method of Estimating Moisture in Superphosphates and Similar Fertilisers," by John Ruffle, F.C.S. "Further Notes on English-grown Tobacco," by A. Wingham, F.C.S.
TUESDAY, 17th.—Institution of Civil Engineers, 8.
—— Pathological, 8.30.
—— Royal Institution, 3. "The Modern Physiology of the Brain, and its Relation to the Mind," by Prof. Victor Horsley, F.R.S.
—— Society of Arts, 8. "The West Indies at the Colonial and Indian Exhibition," by Sir Augustus Adderley.
WEDNESDAY, 18th.—Society of Arts, 8. "Progress in Telegraphy," by W. H. Preece.
—— Meteorological, 7.
—— Pharmaceutical, 11. (Anniversary).
THURSDAY, 19th.—Royal Institution, 3. "The Chemistry of the Organic World," by Prof Dewar, F.R.S.
—— Chemical, 8. "The Formation of Hyponitrites," by Wyndham R. Dunstan and T. S. Dymond. "Ozone from Pure Oxygen," by W. A. Shenstone and J. T. Cundall. "On Thermal Results of Neutralisation and their bearing on the Nature of Solution, and the Theory of Residual Valency," by S. U. Pickering. "Action of Metallic Alkalates on Mixtures of Ethereal Salts and Alcohols," by Prof. Purdie.
FRIDAY, 20th.—Royal Institution, 9. "Bridging the Firth of Forth," by Benjamin Baker, M.Inst.C.E.
SATURDAY, 21st.—Royal Institution, 3. "Victorian Literature," by Prof. John W. Hales, M.A.


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THE CHEMICAL NEWS.

Vol. LV. No. 1434.

## NOTE ON THE SPECTRUM OF DIDYMIUM.

By CLAUDE M. THOMPSON, M.A., D.Sc.

It is well known that the absorption spectrum usually ascribed to didymium shows six bands in the blue and violet with approximate wave-lengths, 482, 476, 469, 462, 444, 428, according to Lecoq de Boisbaudran.

The evidence that we at present possess shows, I think, that these bands belong to at least five different fractions of didymium.

Welsbach (*Monatshefte*, vi., 477) has shown that the band 428 occurs in the absence of all the others mentioned above in the spectrum of the fraction which he names neodymium. On the other hand Crookes (*Proc. Roy. Soc.*, 1886, 502, Fig. 1) has shown that all the other bands of neodymium can be obtained in the absence of the band 428. This band, therefore, belongs to a distinct fraction, and should be obtainable quite by itself.

Crookes has shown that the band 444 varies in strength independently of all others, and is therefore distinct. The same conclusion is arrived at by a slightly different argument. Welsbach's praseodymium shows the bands 482, 469, and 444, together with a faint band in the orange. Crookes (*Ibid.*, Fig. 1) has shown that 482 and 469 can be got in a fraction which does not show 444. It is possible that the faint orange band of praseodymium belongs to the same fraction as 444, since its presence or absence would make little difference in the appearance of the dark orange band of the ordinary didymium spectrum, one part of which it forms.

The band 462 is shown to be distinct by a comparison of Crookes's Figs. 1 and 2, taking into account that 444 and 428 have been shown to be distinct.

The two bands 482 and 469 seem always to accompany each other. They occur together in Welsbach's praseodymium and in all the spectra of didymium fractions published by Crookes. They are distinct from 476, since they occur in praseodymium in the total absence of 476. They may belong to the same fraction as the faint orange band of praseodymium.

The band 476 does not occur in Welsbach's neodymium spectrum.

In fact the two bands 476 and 462 seen in the didymium spectrum are not accounted for by Welsbach at all in the spectra of praseo- and neodymium. Since 462 is distinct, 476 must also be distinct.

I have repeated Welsbach's experiments up to a certain point, and can confirm his results as regards praseodymium in every respect. There is no indication whatever that the three main bands belong to different fractions. I have not been able to satisfy myself quite that the faint orange band of praseodymium really belongs to the same fraction as the others, even supposing that the method of fractionation is not changed. In the didymium spectrum the orange band is much darker than the green, and the difficulty of getting a really concentrated praseodymium solution, which does not show a trace of the green band, is extreme. A small remnant of some other fraction of didymium might therefore cause a faint band in the orange some time after the band in the green had disappeared. Nevertheless, there is no doubt that, by Welsbach's method the orange didymium band is split up, for the maximum absorption with didymium is not at the point in the orange where the band of praseodymium occurs.

I have not yet obtained the neodymium fraction free rom praseodymium, but I have no reason to doubt that Welsbach's observations are correct. A study of the intermediate fractions brings out a point which Welsbach does not refer to. As we pass from the praseodymium end the bands 482 and 469 become fainter, whilst 476 and 462 first appear and then grow stronger, till they become distinctly stronger and much broader than 482 and 469.

It appears then that the absorption spectrum of didymium is splitting up just as the fluorescent spectrum of yttrium is. I have only discussed a few of the bands, but there is no doubt that the other bands will also in time be separated. Indeed, this separation has already been partially effected by Crookes for some of the bands in the red.

Perhaps the most surprising result arrived at by Crookes is that the splitting up of the fluorescent yttrium spectrum is unaccompanied by any change in the spark spectrum. On the other hand Welsbach states that the spark spectra of praseo- and neodymium are parts of the didymium spectrum, and that though similar in general appearance, they are really quite distinct. There does not appear to be any theoretical reason for this difference between yttrium and didymium, and it is to be hoped that the different fractions of didymium will be got pure enough to show whether the spark spectra can be still further split up.

University College, Cardiff.

## ON A FUNDAMENTAL LAW OF THERMO-CHEMISTRY.

By SPENCER U. PICKERING.

My attention has been called to a paper which appeared in the Chemical News, vol. lv., p. 144, under the above title, in which the author arrives at the conclusion that each atom has a constant "thermal equivalent" or heat of combination, when the different atoms are compared under similar conditions. These "equivalents" he calculates for the various atoms, and then proceeds to show that the heat of formation of compounds as calculated from the constants agrees very closely with the observed values. The way in which the constants are calculated is as follows:—

"[H,Cl]Aq = 39·315 [H,Cl,Am]Aq = 53·691
[4Am,3Cl] = 124·661

Now assuming the truth of the law that the radicals liberate or absorb the same amount of heat in all cases, we may write H + Cl = 39·315, H + Cl + Am = 53·691, 3Cl + 4Am = 124·661, whence we get H = 16·963, and Cl = 22·352.

Again, knowing Aq[H,Br] = 38·370, we may by hypothesis put H + Br = 28·370, whence Br is 11·407.

In a similar way we get I = − 3·793.

Again, from the heats of formation of the chlorides of various metals, we may easily obtain their thermal equivalents. Thus, the heat of formation of calcic chloride being 187·600, we may put Ca + 2Cl = 187·600, whence we find the thermal equivalent of Ca = 142·896. In this way I have calculated the thermal equivalents of Li, Na, K, Ca, Sr, Ba, Mg, Cd, Zn, Al, Ni, Co, and Cu".

Now if the above law is true we ought to be able to calculate the heat of formation of the bromides or iodides of any of these metals by simply adding their thermal equivalents. The following are a few of the experimental and calculated results:—

| Calculated. | | Experiment. |
|---|---|---|
| K + Br | = 90·225 | Aq[K,Br] = 90·230 |
| Na + Br | = 85·565 | Aq[Na,Br] = 85·580 |
| Ca + 2Br | = 165·700 | Aq[Ca,$Br_2$] = 165·800" |

I give the quotation in full, since I am utterly incapable of understanding how the three equations can be combined so as to yield the results indicated, or indeed any results of a simpler nature than the algebraic sum of six or seven unknown quantities; this much, however, I do under-

stand, that whatever values the author had taken for the last two reactions mentioned above, and whatever values he had, consequently, obtained for H and for Cl, he would have arrived at precisely the same results. The whole performance is, in fact, nothing but a conjuring trick with the fact that there is a constant thermal difference (in dilute solutions) between two similar radicles, independent of the nature of the other radicle with which they may be combined; the "calculated" values are merely a reproduction of the experimental values, *plus* a small amount of error accumulated during the arithmetical processes through which they have passed. I should recommend the author to turn to CHEMICAL NEWS, vol. liv., p. 217, where he will find a dictum of Professor Armstrong's which may apply in the present case: "Put not your faith in constants."

## VAPOUR DENSITIES.

By THOMAS T. P. BRUCE WARREN.

SOME time ago I wrote an article on this subject, which I intended as a companion paper to an article "On a New Form of Combustion Tube," which appeared in the CHEMICAL NEWS (June 12, 1885).

As some correspondence on this subject appeared in recent issues of this Journal (February 11 and 18), which reminded me of what I had written, I searched for the MS., which unfortunately has been lost.

The apparatus which I have used (Victor Meyer's tube) has a delivery tube with two bulbs, instead of the straight tube as figured in Sir Henry Roscoe's "Chemistry." This form was taken from the apparatus used at South Kensington, and due I believe to Prof. Hodgkinson; however, I can speak very favourably of this modification of the delivery tube.

Mr. Cetti made three of these tubes for me some two or three years ago, with the South Kensington modification, and, although I have had to use these tubes very frequently, I have not yet met with a mishap or obtained a result which I have had to discard or consider doubtful.

I recognise in the letter which appeared in the CHEMICAL NEWS (February 18), signed N. S. S. (Normal School of Science), an appreciation of the apparatus which it fully deserves.

The modification which I have added is a long perforated cork. The perforation is fitted with a long light stopper, made of tubing closed at the ends. The end of the perforation is loosely plugged with asbestos, so that the small tube containing the liquid whose vapour density is required rests on it, and is pushed down when the stopper is inserted. A good sound cork is preferable to an india-rubber stopper.

The object of this arrangement is that the whole apparatus is made perfectly tight, and the insertion of the tube with liquid can be carefully and securely carried out without the slightest fear of disturbance in the condition of the air in the tube, &c.

It is difficult to make and close such a large opening as the withdrawal and replacement of a cork requires, without involving the chance of escape with very volatile liquids or cooling the air to a slight extent, or even driving a little over into the measuring tube, unless the cork is *precisely* pushed into its previous position.

The small tubes are made by taking ordinary glass tubing about ¼ inch outside diameter, rounding one end and closing it, and drawing the other out into a fine capillary bore. A little experience will enable anyone to make these tubes so as to hold the necessary quantity of liquid. These tubes are filled by slight warming and cooling in the liquid; when quite filled and all air removed they are ready for operation. They should be allowed to cool in the liquid, and, when wiped, handled afterwards by metallic forceps.

A little asbestos is placed in the bottom of the Meyer tube to prevent fracture when the small tube is pushed down. The pneumatic trough consists of a tall cylindrical jar, about 6 inches diameter.

The Meyer tube is first closed, and heated in an oil- or water-bath until no air escapes from the delivery tube. The measuring tube is then clamped in position over the delivery tube, and if no bubbles of air are seen the apparatus is ready for use.

When the expelled air has cooled to the temperature of the water, the measuring tube is raised or lowered until the water-level is the same in the tube and trough.

The tube must not be handled, but should be adjusted by the clamp which admits of being raised or lowered on the stand.

The corrections for differences of temperature and barometer readings are made in the usual way.

The tube from the water-bath should reach some distance up outside the Meyer tube; this prevents draughts, and keeps the tube at a constant temperature. An iron tube, about 2½ inches diameter and 24 inches long, closed at one end by welding, forms a convenient vessel for heating the Meyer tube in.

The tube is heated by a large Bunsen burner with a good supply of gas, and whilst the operation is going on every movement which might create a draught must be avoided.

## ON CHECKS IN ANALYSIS.

By W. A. DIXON, F.I.C., F.C.S., Sydney Technical College

IN the numbers of the CHEMICAL NEWS lately to hand there are reports of the American Association of Agricultural Chemistry on methods of analyses. Certain methods are made official for the year in America, but it seems to the writer that—however good the methods may be—there is no certainty of an approach to absolute accuracy when the work is done by different hands.

Perhaps the most accurate commercial work required of any chemist is the assay of gold, and this accuracy is obtained by a system of checks, so that, although the actual weighings of different assayers on a particular sample of gold would give different results if reported directly, the results come to be closely accordant when each corrects his weighings by his own check.

The system of checks seems never to have been adopted in general chemical analysis; at least its adoption has not, so far as I know, been made public, although there has been wrangling enough about the value of different processes, any one of which would be good enough with a check. There is no reason why it should not be used in all determinations where extreme accuracy is required, and it is the only method by which such accuracy can be attained, as all such sources of error as solubility of a substance in water, reagents, &c., are thrown on the check. Some men can succeed better with one process, some with another, and if checks were used the results would be comparable one with another.

I may give, as an example of the method in analytical work, a determination of arsenic as ammonio-magnesian arseniate, for which I first used it. This salt is somewhat soluble even in ammoniacal water, and Fresenius gives a correction to be applied to the mother-liquors, which, however, is inapplicable to the washings,—so this source of error remains, whilst the first is variable with the temperature. The mineral was treated with nitric acid and evaporated nearly to dryness, and then treated with a known volume of water having some arsenic acid in solution. To an equal volume of the arsenic acid solution was added approximately as much chloride of iron as there was of iron in the actual determination; then to each solution were added similar quantities of citric acid, ammonia, and magnesia mixture. The solution and precipitate were treated exactly alike as to

standing, washing, and ignition; first alone, afterwards with starch, and, the magnesia being weighed, the difference between the two gave the datum for calculating the arsenic. The only source of error that arises in this process is that—because of the greater surface of the ammonio-magnesian arseniate in the actual determination—more of the precipitate would be taken up by the wash-water than in the check. This was neglected, but could be checked by using double the wash-water in a second determination.

Examples might be multiplied, but it would be useless, as any one can arrange checks for the work to be done.

This is altogether different from doing a blank experiment, as a blank result may only show the uselessness of the method or worker. It agrees rather with what Kohlrausch ("Introduction to Physical Measurements") says about weighing:—"It is, as a rule, better to make a measure depend not on a trial whether two quantities are equal, for equality is only approximately attainable, but as a trial how much they differ."

## NOTE ON THE SEPARATION OF ACETIC AND FORMIC ACIDS.

By D. S. MACNAIR,
Lecturer on Chemistry in Allan Glen's Institution, Glasgow.

The method usually recommended for the detection of acetic acid in presence of formic acid, by destroying the latter by digesting the mixture with mercuric oxide, is somewhat tedious and unsatisfactory. The following method gives good results, and may be used both for the detection and for the quantitative estimation of acetic acid in presence of formic acid.

The substance to be tested is distilled with dilute sulphuric acid, and the distillate, containing the free acids, is then boiled for ten minutes in a flask provided with an inverted condenser,* with an equal bulk of chromic acid mixture (made by dissolving 12 grms. of potassium bichromate in 30 c.c. of sulphuric acid diluted with 100 c.c. of water). By this treatment the formic acid is readily and completely oxidised to carbon dioxide and water, while the acetic acid remains unchanged. The liquid is now distilled, and in the distillate acetic acid (if present) is readily detected by neutralising and adding ferric chloride.

In the following experiments weighed quantities of the pure anhydrous acids were taken, the formic acid destroyed as described, and the acetic acid distilled off and determined by titration with standard alkali:—

| | Weight of acetic acid taken. | Found. |
|---|---|---|
| I. | 1·076 grms. | 1·056 grms. |
| II. | 1·171 „ | 1·150 „ |

## DEPOSITS OF PHOSPHATE IN ITALY.

By KONRAD WALTER, Engineer.

Considering the serious complaints of capitalists and manufacturers in the most industrial countries of Europe, concerning the continually increasing competition in trade, it might be well to direct their attention to Italy. This country is rich in mineral treasures, but the enterprising spirit of the Italians is not as yet sufficiently awake to take new things in their own hands; they prefer to follow the beaten tracks.

There is no doubt that the mining of metallic minerals in Italy has taken a great development in the last thirty years,—mostly with foreign capital and energy,—but this branch of industry suffers also more or less at present, though there are still many fine enterprises concerning mining business which might be pointed out.

The mining of different other minerals—as phosphates, fireclay, &c.—has likewise not as yet found the consideration due to it, and on those enterprises the attention of capitalists is chiefly to be directed.

There is no doubt that Italy always has been, and is still, an eminently agricultural country. However, rents have recently been going down in a most surprising degree, and this for a simple reason,—because there is no proportion between what is taken year by year from the soil and what is replaced by natural stable manure.

Efforts have been made, chiefly in the North of Italy, to meet this increasing retrogression of the productivity of the soil by means of artificial manures. The results have been of course very satisfactory, but they are paralysed by the high price of the artificial manures, which—and this mostly in the South—have to be imported from other countries. Though many manure works have been erected, the misproportion of the price of manures (chiefly of phosphoric acid) for agriculture still exists. This is shown by the great importation that takes place. Up to now *all mineral phosphates* are imported, and the price of sulphuric acid is still much too high.

Some years ago there was discovered in the South of Italy, near Gallipoli, and directly on the sea-shore, a very considerable deposit of natural phosphates, comprising many millions of cubic feet. This deposit is laying with the outcrops quite on the surface, while the lower strata are falling off to the sea. In geological position this layer belongs to the Eocene formation. In this brittle limestone there are imbedded a great quantity of coprolites, together with bones and other remains of antediluvial animals. According to different trials that were made it appears that about 50 per cent of the whole layer consists of phosphates. The latter are easily separated from the chalk, and contain 35 to 38 per cent of phosphate of lime. If burnt in a limekiln, and separated by hand in a very rude manner, they give a phosphate of 50 to 55 per cent. It is to be remarked that those trials were made with some hundred tons, taken *directly from the surface*, which had been exposed from time immemorial to the action of atmosperic influences and infiltration of carbonate of lime. There has never yet been made any trial to bring up, by boring, samples from deeper layers, which would surely be richer. But, considering the excellent position, comparatively cheap coal, and cheap labour, even the above crude process of enriching the poor phosphates would give excellent results. It would be quite wrong to attempt exportation of these phosphates; the most rational way would be to transform them on the spot into superphosphates. Those latter are easily sold in any quantity in the country itself.

As for the manufacture of sulphuric acid (for this transformation) it is to be mentioned that this might also be made on the spot at exceptionally low cost price, considering that it would be gained as a secondary product.

Rich and poor sulphur ores can be had in unlimited quantities. By using the patent furnace of M. Konrad Walter, chemical engineer in Milan, out of the sulphur ore can be got not only the sulphur, as up to now in the "Calcaronis," but also the sulphurous acid gas in a regular concentrated stream. This latter is to be utilised for the manufacture of sulphuric acid.

(Of the sulphur contained in the natural sulphur stone about 62 per cent are obtained in the now commonly used "Calcaronis"; the remainder goes into the air as sulphurous acid gas.)

As the whole enterprise would be on the sea coast, the transport to all parts of Italy would be much facilitated. Along with the superphosphate a good deal of sulphuric acid might be placed in commerce in the South of Italy, where it is used in considerable quantities by oil-refiners,

* Unless the amount of acetic acid is to be determined quantitatively the condenser may be replaced by a straight glass tube of abou 7 m.m. diameter, and not less than 70 c.m. in length, which should be fitted to the flask by a cork.

dyers, petroleum-refiners, &c. Hitherto prices as high as 70 frs. per ton of acid of 1·7 sp. gr. are paid, while the cost price of this acid made in the above-mentioned manner would not exceed 2 frs. all included.

Besides this, the low cost price and favourable position would even permit of a successful exportation to Southern France, Tunis, Levant, Russia, and Roumania, where the use of those articles is every day increasing.

It is a well-known fact that the Italian Government offers all facilities for the development of national industry, and therefore any such enterprise would find the greatest protection.

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## NEW SUGAR REACTIONS.

By DAVID LINDO.

THE following paragraph appeared in the *Lancet* of January 8th, under the head of "Two New Tests for Sugar":—

"At a recent meeting of the Vienna Chemico-Physical Society, Dr. Hans Molisch, Assistant at the Phyto-Physiological Institute of Vienna University, described two very delicate tests for detecting sugar in liquids. The reactions employed are the following:—A half cubic centimetre of the liquid containing sugar is mixed with two drops of an alcoholic (15 to 20 per cent) solution of α-naphthol; then concentrated sulphuric acid is added in excess. In presence of sugar the liquid, if shaken, assumes immediately a deep violet colour, and by adding water to the liquid a blue-violet precipitate is formed. In the other reaction thymol is employed instead of α-naphthol, and the liquid containing sugar assumes a carmine-red colour. These reactions are more delicate (as was shown by experiments) than our common sugar-tests, and are successful with most kinds of sugar; they can be also used for proving the presence of sugar in the tissues under the microscope. It was shown also that normal urine of man without any preparation gives the reaction, even if diluted with water to the extent of from 100 to 300 times its volume, and therefore the suggestion that normal urine contains sugar seems to be proved. If normal human urine is diluted with water to more than 300 times, it fails to give the reaction, while urine of diabetic persons can be diluted to a higher degree to exhibit the reaction with α-naphthol."

How the tests are to be applied for proving the presence of sugar in the tissues under the microscope is not apparent. It will be observed no reference is made to the fact—perhaps because considered too obvious to need it—that if the liquid under examination contains any substance convertible into sugar by the action of sulphuric acid and heat, the reaction will be obtained as if sugar had originally been present; yet this must surely greatly reduce the value of the reaction as a test for sugar.

I have made some experiments with the thymol test, but not with α-naphthol, for want of the reagent. Fifteen grms. of thymol were dissolved in alcohol, the volume made up to 100 c.c., and 2 drops of this solution used in each experiment. The quantity of liquid taken for testing was always half a c.c., and of strong sulphuric acid 1 c.c. The acid must be quite free from oxides of nitrogen, or a mistake may easily be made, as will be explained further on.

Dilute starch paste (1 per cent starch) gave a very fine reaction with the test, and a 1 per cent solution of gum arabic (fresh) a very good one. The colour was intense red with the gum at first, but became brownish after a little time from charring. On diluting with 10 c.c. water, and stirring, a fine purple-red precipitate formed in the starch tube, and a dark purple one in the gum. This precipitate is by far the most characteristic feature of the reaction, and will be more fully referred to presently.

One part of cane-sugar in 200,000 parts of distilled water gave a distinct reaction, but none could be obtained with 1 part of sugar in 500,000 parts of water.

All these experiments have been several times repeated; the results were found to be somewhat irregular. Thus with a dilution of 200,000 a tint was sometimes obtained that could not be distinguished from the colour produced with a dilution of 100,000. This is owing chiefly to variations in the rise of temperature that occurs on adding the acid, and cannot be guarded against whatever precautions may be taken.

All samples of normal human urine examined gave the reaction (or one very similar to it) when undiluted, and most of them when diluted with 50 volumes of water. In the undiluted state the reaction was sometimes greatly obscured by charring, but on diluting the product with 20 c.c. of water the purple tinge was always observable, and a purple precipitate fell after some time. When the urines were subjected to the action of sulphuric acid alone, and the products diluted to the same extent as those in which thymol had been used, the difference was very striking, the precipitates being devoid of any purple tinge.

Yet all this, I think it will be pretty generally considered, falls far short of proving the presence of sugar in normal urine,—a complex fluid, which must be acted on by such a potent agent as concentrated sulphuric acid to bring about the reaction.

As our knowledge respecting the nature of these reactions is very imperfect, notwithstanding that attempts have been made by capable observers to explain some of them, it would be unsafe at present to affirm, even, that what occurs with urine on applying the test to it proves that a sugar nucleus at least must be present in the secretion.

I have cautioned against the use of sulphuric acid containing oxides of nitrogen in trying these experiments, the reason being that these bodies, as is very well known, give colour reactions with thymol in the presence of strong sulphuric acid, and some of these reactions cannot be distinguished by the eye from the reaction produced by sugar.

I met with a sample of commercial sulphuric acid containing so much nitrous, that, on adding a little to 2 drops of thymol solution in a test-tube, and shaking, the liquid assumed a bright emerald-green colour; on adding a little water, and shaking, the colour changed to red. If in testing for sugar the reagents had been mixed in this order, the fact that there was something wrong with the acid would have been apparent before adding the liquid under examination; but if half a c.c. of distilled water had been added to the thymol instead of sugar solution, and then the sulphuric acid, a bright red colour would have appeared at once, as if a dilute sugar solution had been used.

If a very dilute solution of nitrite of potassium—say 0·3 grm. in 100 c.c. water—is employed in place of a sugar solution (say ¼ per cent), and used in the same way, the colour reaction obtained with the nitrite will be undistinguishable from that produced by the sugar. On diluting the nitrite product with 10 c.c. water, a purple precipitate may possibly form, though it is not often obtained under the conditions of the experiment. This precipitate is thymol dye, and closely resembles in appearance some of the precipitates obtained in sugar testing. They are easily distinguished by collecting on small filters, and, after washing, adding a small quantity of alcohol. The sugar precipitate dissolves, and the colour is instantly destroyed.* The nitrite precipitate dissolves in the alcohol, forming a beautiful purple solution.

Thymol is not the only stearoptene that yields, with sugar and concentrated sulphuric acid, an intense purple-red product. Kingzett states that common laurel cam-

* At least the purple will no longer be recognisable. This may be due to impurities, which, in testing for sugar as described, it may be safely assumed will always be present in the precipitate.

phor, dissolved in sulphuric acid, gives with sugar a most beautiful colour reaction,—a statement I can fully confirm, though I have not been able to render this camphor available for showing the presence of sugar in highly dilute solutions. Menthol I find gives a splendid reaction, an alcoholic solution being used in the same way as thymol. The solution, however, must be much weaker, 1 grm. of menthol dissolved in 100 c.c. alcohol being strong enough for the purpose.

Half a c.c. of sugar solution, 1 part in 40,000 parts of water, gives a very distinct reaction with this reagent. The menthol used was in crystals resembling in appearance magnesium sulphate.

On adding water, however, to these coloured products from common camphor and menthol, the colours are at once destroyed; there is no characteristic precipitate formed as with thymol, which on this account is decidedly to be preferred as a reagent in testing for sugar.

It is pretty evident these colour reactions are not brought about by the glucose acting as a reducing agent, since with no other substance tried that acts as such have I succeeded in producing them.

The presence of sugar when mixed with glycerin is easily shown by these tests; the glycerin should be mixed with about ten times its volume of water before applying them.

When the reactions have been more closely studied they may find a useful application in revealing the presence of the sugar nucleus in the glucosides. The only one I have tried as yet is salicin, a small quantity of which was boiled in dilute sulphuric acid a few minutes, and the solution tested. Very good reactions were obtained with the thymol and menthol tests.

Kingzett and Hake have shown* that if the purple product formed by mixing ordinary camphor, sulphuric acid, and sugar solution together, is diluted largely with water, the colour is destroyed, but a precipitate forms which if separated and treated with concentrated sulphuric acid developes again the intense purple colour. The following experiment shows the same occurs with menthol:—

*Experiment.*—Five c.c. cane sugar solution (1 per cent) was placed in a small beaker, 1 c.c. menthol solution (5 grms. in 100 c.c. alcohol) added, then 10 c.c. strong sulphuric acid. The mixture was shaken, and after a few minutes poured into 200 c.c. water. The liquid became turbid, and the colour light yellowish brown. It was filtered at once; the filtrate was clear and almost colourless. The precipitate on the filter, having been first washed with about 100 c.c. water, was treated on the filter with alcohol. The alcoholic solution had a pale yellowish brown colour. It was evaporated at a gentle heat nearly to dryness, and strong sulphuric acid added to the residue: a magnificent purple colour was at once developed.

Altogether the subject is a very interesting one, and chemists should feel grateful to Dr. Molisch for having by his discovery recalled their attention to a class of reactions the correct interpretation of which may lead to results of considerable importance to Science.

Falmouth, Jamaica, B.W.I.,
April 11, 1887.

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**Final Reaction in Titrating with Fehling's Solution.**—E. Beckmann.—The author refers the difficulty of detecting the exact point when the blue colour disappears to an optical deception. A liquid in which a yellow precipitate is suspended is very likely to assume the complementary colour. The best method for avoiding this deception is to titrate until a portion of the liquid, when filtered off, no longer gives the reaction of copper.—*Zeit. Anal. Chem.*

* Kingzett, "Animal Chemistry," page 421. They used a freezing mixture in some of their experiments, and added the sugar solution drop by drop to prevent charring.

## THE SAMPLING OF CAST-IRON BORINGS.*

By PORTER W. SHIMER, M. E., Easton, Pa.

As is well known, cast-iron borings are a mixture of small particles of iron with more or less of finely divided graphite, separated from the surfaces of these small particles during the process of boring. The amount of graphite thus mechanically mixed is, in all cases, quite large enough to cause serious difficulty when the problem is to obtain an average sample of a given lot of borings for carbon determination. This difficulty arises from the necessity of obtaining a uniform mixture of the heavy and comparatively coarse borings with the finely divided and light graphite, and of removing a sample for analysis without disturbing the uniformity of this mixture.

It was first sought to overcome this difficulty by having the borings made very fine, so that they might have more nearly the size of the particles of graphite. It was not practicable, however, to secure this uniformity of size, since much of the graphite is in the form of the finest dust. At all events, the duplicate determinations of carbon in these fine borings, made with every precaution by combustion in oxygen, frequently showed differences too large to be accounted for in any other way than by imperfect sampling.

Very coarse borings were also tried with the idea that the graphite separated from these large and heavy pieces would, perhaps, be inappreciable; but it was found that quite enough was separated to vitiate the results.

Various methods of mixing were tried, both in the bottle and on glazed paper; but in all these mixtures it was found that duplicate samples seldom contained the same proportion of the mechanically mixed graphite; and when they did, there could be no certainty that it was the true proportion. All this was shown many times over by the failure of duplicates to agree closely, the difference being sometimes so much as 0·20 per cent. It was finally clear that nothing was to be hoped from these methods. Even if we could secure a perfect mixture containing in every part its due proportion of graphite, it would run a great risk of being destroyed the moment a spatula was inserted to remove a sample: for the least agitation causes some of the graphite to fall through between the coarser borings.

The sampling diffculty was finally overcome in this way: The borings are carefully poured out into a large porcelain crucible or dish, and enough alcohol is added to merely moisten them (2 c.c. alcohol to 30 grms. borings). Mix thoroughly for about five minutes. Remove with a spatula as many samples of the moist borings as are needed, weighing them out roughly so as to get approximately the weights desired. Dry off the alcohol and weigh accurately. The samples thus obtained perfectly represent the average of the original sample, for the alcohol simply serves temporarily to hold the graphite where it belongs, upon the surface of the borings.

As the alcohol evaporates from the original sample the graphite agains falls away from the borings, and the moistening must be repeated when new samples are to be removed.

It is not at all difficult to obtain alcohol sufficiently pure for this purpose. An estimation, based on a determination of the carbonaceous residue left on evaporation, showed that the alcohol used in these experiments would cause an error which would not appear until the fifth decimal place in the percentage of carbon. I have made many duplicate carbon determinations since using the moist sampling method, and have had none but satisfactory results, having never found a greater difference than 0·03 per cent between duplicates. Generally the difference is from 0·01 to 0·02 only.

The following total carbon results show the improvement:—

* *Transaction of the American Institute of Mining Engineers*, Pittsburgh Meeting, February, 1886.

| | I. | II. |
|---|---|---|
| Mixed dry in the bottle .. .. .. | 3·68 | 3·84 p.c. |
| Moistened with alcohol and mixed .. | 3·97 | 3·99 |

The first results are an extreme case of unsatisfactory duplicates; and they also show the tendency of the graphite to go to the bottom of the bottle when mixed dry. The mechanically mixed graphite, approximately determined by removing the iron by means of a magnet from samples taken moist, was 0·76 and 0·79 per cent in duplicate determinations.

After shaking up the dry borings a few times, and removing nearly all from the bottle, the remaining sample contained 1·29 per cent mechanically mixed graphite.

The other determinations, such as phosphorus and silicon (iron excepted), are, perhaps, not appreciably affected when samples are taken dry. But whenever samples are thus taken, the borings which remain are for ever vitiated for carbon determinations which shall truthfully represent the original sample. In very careful work, therefore, and especially when there is any prospect of subsequent carbon determinations to be made, it is neccssary to moisten the borings when weighing out samples for phosphorus and silicon, or to have two sets of borings made, one of which is to be reserved for carbon determinations. For iron determinations the samples should always be taken moist.

It was suggested by Mr. Frank Firmstone, Superintendent of the Glendon Iron Works, to determine whether or not there is any appreciable loss of graphitic dust while making cast-iron turnings according to the method devised by him, in which the turnings are taken equally from the whole section of a piece of pig-iron, the outside being first removed. Through the kindness of Mr. Firmstone, I was enabled to procure from the same piece of pig-iron a sample of turnings taken dry, a second sample kept moist with alcohol to prevent loss of dust, and several sections $\frac{1}{2}$ inch in thickness.

The following are the total carbon results from these samples:—

I. Turnings taken dry, but sampled moist.
II. Turnings taken moist.
III. Thin section.

| I. | II. | III. |
|---|---|---|
| 4·132 | 4·122 | 4·031 |
| 4·123 | 4·123 | 4·038 |
| 4·111 | 4·103 | 4·108 |

The results under I. and II. show that, with care in catching the turnings, and avoidance of drafts of air, there is no appreciable loss of graphitic dust. The first two results on the thin section are low, because of incomplete decomposition of the iron, when, after forty hours, hydrocloric acid was added to complete the solution. The third result is about right; but complete decomposition was obtained in this case by frequent and long-continued stirring. While, therefore, it is possible to obtain the correct total carbon by use of a thin section, it offers no advantage in point of time; since borings may be dissolved in neutral and cold copper and ammonium chloride solution in fifteen to twenty minutes by constant stirring.

Some chemists, with a keen appreciation of the sampling difficulty, have proposed to overcome it by using clippings of the iron from $\frac{1}{8}$ to $\frac{1}{10}$ inch in thichness. While it is no doubt possible, in most cases, to obtain the true result by this means, it is open to the objection of being very slow when these clippings are to be dissolved in neutral copper and ammoninm chloride solution. Furthermore, the weight of iron taken for carbon determination in cast-iron being limited by convenience to about 3 grms. a very few clippings make up this weight, and these represent only those parts of the sample from which they happen to come. While there may not be an appreciable difference in the composition or in the condition of the carbon of the different parts of a section of pig-iron, it is yet possible that there may be; and in this case it is easy to be on the safe side.

When turnings are taken equally from the whole section of a piece of pig-iron, and are then moistened with alcohol and thoroughly mixed, every part of the section has its due representation in a sample of 3 grms.

It may not be out of place to add, that in sampling ores, and, in fact, any similar mixture of particles of different size, composition, and specific gravity, I am now accustomed to moisten with water before mixing. This secures a uniform mixture of coarse and fine parts from which a true sample can easily be removed, prevents loss of dust, and is in every way more satisfactory than mixing dry.

In pulverised ores it is very commom for the finest part to consist principally of lighter gangue material; and the problem of securing a true sample of such a mixture is similar to that of obtaining a true sample of a mixture of cast-iron borings and graphite.

# PROCEEDINGS OF SOCIETIES.

## PHYSICAL SOCIETY.

*May 14th*, 1887.

Prof. W. E. Ayrton, Vice-President, in the Chair.

Mr. T. Mather was elected a member of the Society.

The following papers were read:—

"*On a Modification of a Method of Maxwell for Measuring the Coefficient of Self-Induction.*" By E. C. Rimington.

The method referred to is given in Maxwell's "Electricity and Magnetism" (vol. ii., § 778), and is called "Comparison of the Electrostatic Capacity of a Condenser with the Electro-magnetic Capacity of a Coil." The apparatus used consists of a Wheatstone's bridge having the coil in one, and the condenser as a shunt to the opposite, arm. In order that no deflection may be produced, either for steady or unsteady currents, a troublesome double adjustment of the resistances is necessary, and to obviate this the modification was devised. It consists in placing the condenser as a shunt to only part of the arm, and this part can be varied by sliding contacts without altering the whole resistance of the arm. An ordinary resistance balance for steady currents is first obtained, and the sliders are then adjusted until no deflection is produced on breaking the battery circuit. Under these circumstances it is shown that—

$$L = K r^2 \frac{D}{B},$$

where K is the capacity of the condenser, $r$ the resistance between the sliders, and D and B the resistamces of the arms in which the coil and condenser are placed. The conditions of maximum sensibility are investigated, and also those under which a telephone may replace the galvanometer. In the latter it is shown that the only possible solution is when $r = B$, *i.e.*, Maxwell's arrangement. The author believes his modification would be made much more sensitive by adopting the "cumulative" method used by Profs. Ayrton and Perry in their secohmmeter, and in his case neither the speed nor the "lead" need be known.

Mr. W. N. Shaw asked whether any serious difficulties were experienced with telephones, owing to electrostatic capacities of wires, &c.; and Mr. W. E. Sumpner pointed out that the particular arrangement given in Maxwell is not always the most sensitive, as was shown in his remarks at the last meeting of the Society of Telegraph Engineers.

Mr. Bosanquet thought the method a valuable one, and hoped many experiments would be made on coils whose coefficients were calculable, in order to find out the differences between calculated and observed results.

Prof. Ayrton referred to the paper by Prof. J. J. Thompson in the *Philosophical Transactions*, and pointed out that the formula there given for the capacity of a condenser in electro-magnetic measure is identical with that given in Maxwell, § 776, when the printer's error of interchanging $a$ and $\alpha$, in the denominator for $R_2$, is corrected.

"*On the Production of Sudden Changes in the Torsion of a Wire by Change of Temperature.*" By R. H. M. Bosanquet, M.A.

A very fine hard-drawn platinum wire, 4 or 5 feet long, was used as a suspension for a ballistic galvanometer, and exhibited peculiar phenomena. The steel needles were replaced by brass ones, and the peculiarities investigated. When the room was warmed the needles swung round nearly 70° for a few degrees rise of temperature, and remained in about the same position for further rise. If it was now cooled a few degrees (3° or 4° F.) they quickly returned to their initial position. The author has not found a complete explanation, but believes it to be due to unequal expansion, and loose contact amongst molecules, and has devised a simple mechanism to illustrate his meaning.

Remarks and suggestions were made by Prof. Perry, Mr. Lant Carpenter, and the Chairman.

"*On a Magnetic Potentiometer.*" By A. P. Chattock. Read by Prof. Reinold.

The "so-called" magnetic resistance between two points on a magnetic circuit may be expressed as the ratio of the difference of potential to the total induction passing from one to the other (provided there be no magneto-motive force between them). From the fact that the volume integral of induction through a wire helix of constant cross section is proportional to the average difference of potential between its ends, it follows that any alteration in that difference of potential will give rise to an electro-motive force in the helix proportional to that alteration. Hence, if the wire be connected to a ballistic galvanometer, the combination may be called a magnetic potentiometer. A helix is formed by winding wire uniformly on a piece of solid india-rubber or canvas gas-tubing, of constant cross section, using an even number of layers to avoid external inductive effects, and leaving a small space between the turns so as to allow the tube to bend without elongating. Experiments made to measure the difference of potential between the ends of a magnet gave satisfactory results. One end of the helix was held stationary at one end of the magnet, whilst the other was moved quickly to the other end of the magnet, and the resulting throw of the galvanometer observed. This was next done at two operations, and the sum of the two throws was very nearly equal to the first. The results can be reduced to absolute measure by passing the helix through a coil of $n$ turns, bringing its ends together, and starting or stopping a current, C, in the coil, the resulting throw of the galvanometer being noticed. The magneto-motive force used in this experiment is $4\pi n$ C.

An interesting discussion followed, in which Prof. Perry, Mr. Shaw, Prof. Ayrton, and Mr. Bosanquet took part, the latter mentioning a measurement of magnetic potential made by himself some years ago.

In consequence of the absence of Prof. S. P. Thompson, his paper on "Secondary Generators" was postponed till next meeting.

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**Influence of Temperature upon Spectroscopic Observations and Measurements.**—G. Krüss.—On elevation of temperature all phenomena of absorption and emission are transposed, in case of glass prisms, towards the violet end of the prism, but in the case of quartz prisms towards the red. These displacements are generally the greater the more refrangible the regions of the spectrum in which they occur.—*Zeit. Anal. Chem.*

# NOTICES OF BOOKS.

*The Printing of Cotton Fabrics.* Comprising Calico Bleaching, Printing, and Dyeing. By Antonio Sansone, late Director of the School of Dyeing at the Manchester Technical School. Manchester: Abel Heywood and Son. London: Simpkin, Marshall, and Co.; and Hamilton, Adams, and Co.

The appearance of this book cannot be pronounced uncalled for. So rapid have been the changes in the tinctorial arts, and so many and varied have been the improvements introduced, that the author is justified in pronouncing that hand-books written a few years ago are now somewhat out of date. Mr. Sansone in the present volume limits his attention to calico printing. Bleaching and dyeing are considered only in so far as they are subsidiary to printing, properly so called. The treatment of silks and of delaines, and other mixed goods, is also not included, though in the Appendix there are a few pages devoted to the printing of woollen tissues, in explanation of some very beautiful patterns sent to the author by M. Horace Kœchlin, of Alsace.

The work opens with a brief history of the art, from which we learn that Manchester is still the largest centre in the world for the production of printed cottons, the number of machines at work in the district exceeding five hundred. Still it is here admitted that the highest grades of printing are executed in Alsace, and that, in spite of the money expended over our schools of art for more than thirty years, "Paris still holds the monopoly for the production of designs, especially of those of the better class and of high artistic value." Surely this fact, taken along with others which have been from time to time noticed in the Chemical News, should lead us, as a nation, to enquire whether our methods of training, as well in art as in science, may not be fundamentally astray?

We note with great pleasure the unqualified statement that "indigo, although seriously threatened by Bäyer's discovery of the synthetic production of indigotine, is now as firmly established as ever, as the artificial product cannot be as cheaply produced as the natural dye-stuff." If we are wise, however, we shall not "rest and be thankful," but strain every nerve to improve the cultivation and the extraction of indigo, so as to furnish a better quality and a larger yield. It is, of course, known to the majority of our readers that indigo occurs in the plant in the state of a glucoside,—the *Indican* of Schunck,—which, by fermentation, is split up into indigo-blue and a peculiar sugar. In connection with this subject Mr. Sansone throws out an interesting suggestion. "It is a question," he writes, "after the indican has been extracted from the plants or leaves, with water containing a small amount of sulphurous acid or a bisulphite, in order to prevent fermentation, if a larger yield could not be obtained by decomposing the indican by means of weak sulphuric acid (as was at one time done in the case of madder for producing garancine), and utilise at the same time the sugar solution for producing alcohol."

It is commonly known that, in the fermentation-blue vats, mismanagement or the accidental introduction of an unwished-for ferment often leads to serious losses. In like manner, false fermentations are not unknown in the extraction of indigo, which in some cases injure the quality of the product, and in others greatly reduce the yield. Now in indigo-dye vats two methods have been brought forward to combat this evil. One process is the so-called hydrosulphite vat of Schützenberger and Lalande, which dispenses with fermentation altogether. The other effects fermentation by means of a pure cultivation not liable to occasion putrefaction.

In the extraction vat we have two parallel methods:—Mr. Sansone's proposal to split up the glucoside by means of sulphuric acid, or, on the other hand, fermentation effected by a pure thorough-bred culture. We trust that

the vast importance of the interests involved will lead our readers to pardon this seeming digression.

Bleaching, with reference to the preparing of pieces for the printer, forms the subject of the first division of the work. In addition to the ordinary process we find here a description of the Mather-Thompson process, that of Prof. Lunge, and of the electrical process of M. L'Hermite. The Mather-Thompson process is said to effect an economy in time and in water, and to punish the cloth less than does the ordinary method. The result, however, is considered not quite satisfactory for a madder-bleach.

We come next to a consideration of the wares used, which are classified as mineral colours, natural organic colouring-matters, coal-tar colours, mordants, dunging-materials, astringents, soaps, oils and oil-mordants, solvents, thickeners, and albumenoid matters. Under all these heads the substances mentioned are those now in regular use, the numerous natural dyes and coal-tar colours which have merely an experimental or a historical interest being omitted.

The manufacture of the different colours, &c., is not, as a rule, discussed at length. An exception must be noted as concerns the manufacture of extracts. The author points out that in the woods, as in indigo, the colouring-matter is generally present in the form of a glucoside; and here, too, he recommends its splitting up by sulphuric acid instead of fermentation. He recommends that more attention should be paid to this "splitting up," as well as to the quality of the water and to the method of effecting evaporation.

The list of mordants has, of late years, been considerably extended. This especially holds good as regards the compounds of chromium and antimony. We are surprised to see, under Copperas, no mention of the most common and extensive method for production,—*i. e.*, by the action of air and water upon the iron sulphide of the coal-beds, commonly known as "brass lumps."

We regret that the author—unlike Hummel, Crookes, Calvert, and in fact almost all writers on chemical technics in this country—recognises, and occasionally uses, the hydrometer scale of Beaumé. To this scale there is the great objection that it does not bear any simple relation to direct specific gravity. In addition there are two, if not three, discordant versions of Beaumé. In the comparative tables here given 50 B. = sp. gr. 1·532, whilst in another table before us it equals 1·490.

We now come to what may be called the most important part of the work, *i. e.*, the processes of printing. These the author divides into two main categories—the printed or direct, and the dyed colours. Under the first mentioned he includes the steam or extract styles, whether involving the use of coal-tar colours, of dyewood extracts, &c., or of mineral colours; the pigment styles, fixed by albumen; the oxidation colours, including aniline black, naphthylamine puces and greys, &c.; and, lastly, direct indigo printing.

Under the dyed colours appear the alizarine dyed colours (old madder styles); the Turkey reds, with discharges; the vatted indigo styles, the design being produced by resists or discharges; and, lastly, the manganese bronzes.

As an introduction to the description of the printing processes we find very practical instructions for testing the wares, mordants, &c., by sample printing, or, we might say, for the general arrangement and management of the laboratory of a print-works. To suit the tastes and requirements of different readers the receipts are given both in English and in French weights and measures. It must be remarked, however, that the receipts play here a less important part than in some works, being given not as hard-and-fast rules, but in illustration of principles.

The machinery and apparatus are, in a separate section, illustrated both with plates and with figures inserted in the text.

The Appendix contains a notice of the attempts made at applying electric action in printing processes, and a description of the patterns of printed woollens supplied by M. H. Kœchlin. The illustrative patterns—thirty-six on calico and six on woollen tissues—are well executed and instructive.

There are introduced nineteen plates and thirteen figures in the text.

Our opinion of this book is most emphatically favourable. It is both instructive and suggestive, and every person connected with the tinctorial arts will find his library incomplete winhout it.

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*Agricultural Research Association.* Circular No. 6. Aberdeen. 1887.

The experimental farm of this Association is at Glasterberry, Peterculter by Aberdeen, and we are glad to see that, although a few disappointments have occurred, the experimental work is proceeding on the whole in a satisfactory manner. It is of course obvious that investigations such as are being carried on here, intended to be exhaustive and conclusive (like so many others before them), cannot be completed in two or three seasons; but it is thought that one or two of the points under examination can be considered better now than later on. The questions here referred to are those dealt with in the first line of the ten experimental plots, and may be stated as follows:—

"Which of the most approved grasses are most useful in regard to earliness, permanence, quantity, and quality of produce: are those deemed bad, really bad?"

Nine different grasses were experimented on, and the condition of each during the whole year was noted and plotted on a curve: three out of these nine,—viz., rye, cocksfoot, and fescue,—when combined in one diagram, are found to give a crop standing above the average line of freshness and healthy condition during the whole year.

The quantity of grass crop was very carefully estimated, and it is found that in every case the second year's crop is very much greater than the first year's, in one case—viz., fescue—the increase being from 5 cwts. to 2 tons 10 cwts.

Experiments made to find which month of the year is most suitable to sowing, showed unanimously that the practice of sowing in the early spring, viz., April, cannot be improved upon. Nature sows in the autumn, but she cannot do otherwise, and her aim of perpetuating the species is secured if "of fifty seeds she brings but one to bear."

Another series of experiments shows that the best depth for sowing grass is 1 or 1½ inches.

Other subjects are under investigation bearing principally on the everlasting question of artificial manures, about which so much has been written by eminent authorities, without even yet satisfying many agriculturists that the advice given is to be relied on. The reason of this apparent indifference to their own best interests is not far to seek: the farmers and stock raisers who are interested in growing good crops have been brought up, so to speak, on the rule-of-thumb principle, and, moreover, they have not the opportunity—and possibly but little inclination—to read what has been done in districts other than their own: the way therefore to make the practice of scientific agriculture universal is to "keep on pegging away," with many experimetal farms, in as many districts as possible, so that the farmers will have brought home to them the truth, that it *does pay* to use chemical manures.

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*Twenty-eighth Annual Report of the Inspector of Milk and Vinegar for the Year* 1886. Boston: Rockwell and Churchill. 1887.

In the year 1884 the number of adulterated samples of milk was 40 per cent, and these were on the average reduced in value 25 per cent, either by adding water or

removing the cream. During the year 1886 the percentage of adulterated samples has been reduced to 18·55, so that it may be fairly admitted that the work done by this department has been of real value to the consumers of this universal article of food. Previous to making the analysis the specific gravity of all the samples is taken, and the approximate percentage of fat as given by Feser's lactoscope is also noted. The analysis is made in the ordinary manner.

The most important step taken during the year has been the attempt to suppress the practice of colouring milk, and it is believed that this is the first systematic attempt made in this direction by milk analysts in any country. The substance used for colouring the skim milk is known as *annatto:* many objections were found to the ordinary method for detecting and estimating this substance, so a process was devised which has after a considerable trial given good results. This process consists in leaving a strip of filter-paper suspended in milk which has been rendered alkaline by the addition of 5 per cent of a solution of carbonate of soda (1 part to 3 parts of water) for twelve hours: after that lapse of time the strip of paper is taken out and washed in cold water, when, if annatto be present in the milk, the paper appears of a pale salmon-colour; if dipped into a solution of stannous chloride the colour developed is decidedly pink. One part in 100,000 is distinctly perceptible by this means.

In the latter part of the Report we find a few pages devoted to the subject of oleo-margarine, more generally known under the name of butterine. A short description of the manufacture is given, and a further refutation is made of the some time popular idea that butterine is made from filthy materials, or that dangerous chemicals are used in its manufacture. As a matter of fact there is very little difference in the compositions of butter and butterine. With regard to digestibility there may be a slight balance in favour of butter, but for supplying the body with heat and muscular energy they are of equal value; and considering that fat is an absolutely necessary article of food, and that there is not enough butter to supply the demand, the man who has discovered a method of rendering a digestible fat equally palatable with, and selling at a price below that of butter, should be looked upon as a public benefactor.

# CORRESPONDENCE.

## THE INSTITUTE OF CHEMISTRY.

*To the Editor of the Chemical News.*

Sir,—The letter of "F.C.S." in Chemical News, vol. lv., p. 223, raises a question which, in the opinion of many, is of great importance to our profession. It cannot be denied that there is a large number of persons possessed of little chemical knowledge and less general culture who occupy positions which should be filled by regularly trained and well-educated chemists, thus lowering the status of the whole body.

The profession of Chemistry is, in its line, as important to the public as that of medicine, pharmacy, dentistry, or law, and it is of general interest that the men entrusted with the analysis of food, drugs, poisons, &c., &c., and those who are placed in charge of large industrial enterprises, should be guaranteed worthy of confidence as much as the members of the professions named.

If the councils of the Chemical Society, Institute of Chemistry, and Society of Chemical Industry would take the matter up and decide on joint action, I think it very probable that a workable system of licence and registration could be agreed on, which would protect the public from inefficient practitioners and raise the status of the profession.

I hope you will open your columns to the opinions of others on this subject—I am, &c.,

Joseph Fletcher.

Dublin, May 14, 1887.

## THE INSTITUTE OF CHEMISTRY.

*To the Editor of the Chemical News.*

Sir,—The discussion as to the nature and utility of the Institute of Chemistry having been revived in your columns, it may not be out of place to relate an experience for which I can vouch personally. I have no desire to bring the names of individuals forward, but am prepared to give you, Sir, the fullest proofs of my statements. I have seen a letter from a practising analyst, who is F.I.C. and F.C.S., in which he quotes 7s. 6d. for the determination of silicon and phosphorus in pig-iron. Comment is of course superfluous, but it would be interesting to know whether the Institute has any power to check the practice of charging fees such as this. As an individual every chemist is a law into himself, but if Fellows of the Institute are equally untrammelled with outsiders, how can the interests of the profession in general be benefitted by the Institute?—I am, &c.,

Not an F.I.C.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Bulletin de la Société Chimique de Paris.*
Vol. xlvii., No. 3, February 5, 1887.

Russian Chemical Society.—Session of April 3/15 1886.—M. E. Andreeff presented some remarks on the teaching of chemistry in the technical schools.

P. Latchinoff describes the choleidanic and pseudo-choleidanic acids, obtained by oxidising cholanic acid with nitric acids. The barium and silver salts and the ethylic ethers of these two acids have been prepared and analysed. The author communicated some new data on the solubility of cholanic acid in water, alcohol, and ether, and on its optical properties $[\alpha]_D = +56° 40'$.

MM. Mikhailoff and Chlopine made a preliminary communication on the gelatinous state of the proteic bodies.

J. R. Tarkhanoff finds that in its natural condition egg-albumen possesses a feebler rotatory power than the filtered albumen no longer containing gelatinous flocks and filaments.

M. Setchenoff remarked that on heating egg-albumen in a vacuum there are obtained gelatinous flocks not easily attacked by pepsine.

M. Socoloff has studied the action of weak alkalies upon nitro-ethane. He considers it proved that the group, $NO_2$, of nitro-ethane resembles neither the group NOO of the ethers of nitrous acid, nor the group $NO_2$ of the nitric ethers, and secondly that nitro-ethane is not a derivative of hydroxylamine.

P. Melikoff sent in a memoir on tiglic acid, which he has treated with hypochlorous acid, obtaining a mixture of two chloroxy-valerianic acids, distinguished by the properties of their zinc salts.

The same author discussed the properties of the chloroxybutyric and bichlorobutyric acids.

M. Sivoloboff described a method for determining the boiling-points of small quantities of liquids.

The fourth part of the journal contains a memoir by P. Orloff on an hexylic glycerin.

Session of May 1/13, 1886.

D. Pavloff communicated, from a letter by C. Winkler, some details on germanium.

He also announced, on behalf of M. V. Sorokine, that on heating isosaccharine with aniline, a compound is obtained, $C_{12}H_{17}NO_5$, in the form of crystalline needles, fusible at 165°.

E. Werner sent in an account of thermo-chemical researches on the substitution of hydrogen by bromine in the aromatic series.

M. Gadziatsky sent in an account of his researches on the isoprene of caoutchouc.

M. Favorsky announced that methyl-ethyl-acetylene (obtained by the action of alcoholic potassa upon propyl-acetylene) and the dimethyl-allylene (derived from trimethy-ethylene) enter into reaction with sodium if heated to 100° in sealed tubes.

M. Latchinoff made a communication on the isocholanic and isobilianic atids, obtained by the oxidation of the choleinic and choleic acids.

M. Kolotoff has obtained nitro-ethane by causing sodium nitrite to act upon potassium monochloropropionate.

M. Rosenblatt sent in a method for the qualitative and quantitative determination of boric acid by means of methylic alcohol.

M. Poehl communicated the results of the analyses of Crimean wines.

M. Rassine sent in a memoir on the isomeric bromonaphthalides.

The following researches were sent in from the chemical laboratory of the University of Kazan :—

Analysis of Mother-waters and of the Water of a Lake near the Springs of Stolypine, by P. Boulitch.

On Oxystearic Acids of different Origins, by A. and C. Saytzeff.

M. Wolkoff has pursued his researches on the action of high temperatures on the primary monatomic alcohols. If absolutely pure they are not decomposed, even at 200° to 300°, but traces of methyl iodide determine their decomposition.

G. Alibegoff made a communication on the compounds of uranium with oxygen and sulphur, and on the methods of separating and determining this element in presence of the alkaline and alkaline-earthy metals. The processes are not given.

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*Zeitschrift für Analytische Chemie.*
Vol. xxv., Part 4.

**Air-Analysis on a Novel Principle.**—Otto Petterson —This memoir cannot be reproduced without the four accompanying illustrations.

**Gas-Analytical Method.** — Otto Petterson. — This memoir also requires the illustrations here given.

**On Normal Solutions.** — L. L. de Koninck.—The writer thinks that Winckler (who has since practically abandoned his proposal) might have done better if he had taken the molecule of hydrogen instead of the atom as the basis of his system.

**Determination of Phosphorus in Iron and Steel.**—E. F. Wood.—The author proposes two modifications in the direct molybdic method of Eggertz, which he considers as the best hitherto known. This paper will, if practicable, be inserted *in extenso*.

**A Novel Method for Determining Fluorine Volumetrically.**—Dr. F. Oettel.—An illustrated paper.

**Separation of Zinc from Iron, Cobalt, and Nickel.** —P. von Berg.—The author, at the suggestion of Prof. Ostwald, has attempted the separation of zinc from iron, cobalt, and nickel, by passing sulphuretted hydrogen into a formic or monochloracetic solution. In presence of only 3 c.c. of free formic acid (sp. gr. 1·2) and 360 c.c. water he obtained zinc sulphide free from any ponderable traces of iron. It is necessary to filter immediately after the treatment with sulphuretted hydrogen, as if it is allowed to stand some zinc sulphide is deposited. The liquid should be heated to 50° to 60°. After the solutions were duly diluted and heated they were mixed with a quantity of sodium formiate approximately equal to half the equivalent of the zinc sulphate present, and with the proportion of free formic acid (sp. gr. 1·2) and a slow current of sulphuretted hydrogen was then introduced until it became predominant. A large excess of sodium formiate is to be avoided. As soon as the liquid had partially settled it was filtered, the precipitate washed with sulphuretted hydrogen water to which about 1 per cent of free formic acid had been added, and the zinc sulphide was determined in the known manner. Zinc may also be successfully precipitated from a monochloracetic solution. The author proceeds in a very similar manner to that already described. As soon as the precipitation is completed and sulphuretted hydrogen predominates he filters at once without waiting for the liquid to become clear. Any portion of precipitate adhering to the side of the beaker is at once brushed off with a feather before it can dry. The precipitate is washed with sulphuretted hydrogen water, to which a little monochloracetic acid has been added.

**Direct Separation of Manganese from Iron.**—L. Blum.—This separation depends on the precipitation of manganese from an ammoniacal solution in which all the iron remains dissolved. Potassium ferrocyanide effects no precipitation in the ammoniacal solution of a ferric salt to which tartaric acid has been added, whilst manganese is thrown down from such a solution as manganese ferrocyanide. The blue deposit of iron ferrocyanide produced by potassium ferrocyanide in the acid solutions of ferric oxide, is decomposed on treatment with alkalies with separation of ferric hydroxide. If the solution in which the decomposition takes place contains a tartrate the ferric hydroxide is dissolved by the latter in its nascent state. Manganese ferrocyanide is not decomposed by ammonia. The separation is carried out as follows :—A hydrochloric solution containing ferric chloride and manganous chloride is mixed with so much tartaric acid that no precipitate appears on adding ammonia so that the reaction is strongly alkaline. The clear solution, containing ammonia in excess, is precipitated with potassium ferricyanide, when all the manganese is deposited as manganese ferrocyanide. If, in addition to manganese, nickel, cobalt, and zinc are present, they also are thrown down as the corresponding ferrocyanides. The precipitate filters badly, passing through the filter unless boiled, and even then the water passes through turbid on washing. The process, however, can be used qualitatively for the detection of traces of manganese in presence of much iron.

**Syrmian Wormwood Wine.**—M. Petrowitsch.—For this memoir we must refer the reader to the original.

**The Determination of Tannin: A Proposal.**—E. B. —After having tried in various modifications, but with unfavourable results, an entire series of the earlier methods for the determination of tannin, Gerland's with tartar emetic, Wolff's with copper oxide, Handtke's with ferric acetate, the author turned to Löwenthal's method as modified by Schroeder. But he could not obtained the "hide powder," needful for precipitating the tannin. Instead of hide powder or its substitutes (the gelatigenous tissue of bones and horn-cores) other precipitants have been used, such as bone-black, glue, and more recently gelatin and common salt. Instead of indigotine, the solution of extract of indigo has been recommended; the untrustworthiness has been shown by Von Schroeder. He also uses ferric acetate as the best means of recognising tannin. The author, in carrying out Handtke's method, found it impracticable as described, since the precipitation of the tannin is too tedious. The precipitation seems, however, complete i the reagent is used in excess. He prepared the solution from iron-ammonium alum, crystalline sodium acetate, enough to saturate the sulphuric

acid combined with the ferric oxide, and a little acetic acid; therefore: iron-ammonium alum, 48·2 grms.; crystalline sodium acetate, 25·0 grms., acetic acid containing 50 p.c. hydrate, 40·0 c.c., all dissolved to 1 litre. Of this solution there was added to Schrœder's tannin solutions or nut gall decoctions (of 5 grms. per litre) 10 c.c. to 50 c.c. of the tannin solution. After a quarter of an hour the author tested if everything was precipitated, which was always the case, made it up to 100 c.c., and filtered. Of the clear and generally greenish solution 20 c.c. were taken (=10 c.c. of the original solution), and after the addition of 20 c.c. solution of indigotine it was titrated with potassium permanganate. The number of c.c. obtained (consumed by matter other than tannin) were deducted from the total c c. found in the first titration, and the remainder was taken as pure tannin.

**Safe Method of Breaking off Glass.**—E. Beckmann.—The author, in case, *e.g.*, of a combustion-tube, operates as follows:—At the part to be fractured there is made a short mark with a file. The tube is wrapped round with pads of moist filter-paper, so that there remains a track of 1 to 2 m.m. in width on both sides of the file-mark. If this space is heated over the Bunsen burner or the pointed flame of a gas blast, while the tube is made to revolve slowly on its axis; there is then formed a smooth ring-fracture in the direction of the file-mark, keeping the exact middle between the two pads. These pads are from 1 to 2 m.m. in thickness, and 2 to 4 m.m. in breadth with the folds turned towards the file-mark.

**Chemical Characteristics of Beers produced with Pure Ferment Cultures.**—E. Borgmann.—It is shown analytically that the two bottom ferments described by Hansen as distinct if introduced into the same nutrient liquid and under identical conditions effect clearly different chemical work. They differ, therefore, not merely botanically, but chemico-physiologically.

**Titration with Weighing of the Liquid Consumed.**—F. V. Pool.—From the Chemical News.

**Contributions to Micro-chemical Analysis.**—A. Streng and K. Haushofer.—Not suitable for abstraction.

**A New Air Thermometer.**—G. Grasi.—This apparatus, the arrangement of which is not described, not merely indicates, but measures temperatures to $\frac{1}{10000}$° C.

**An Improved Thermo-electric Battery.**—Clamond and Carpentier.—Noticed under *Comptes Rendus*.

## MISCELLANEOUS.

**The late Mr. E. O. Brown.**—In our number for December 24th, 1885, we mentioned that a fund was being raised among the friends of Mr. Brown for the object of affording some aid to Mrs. Brown, who had four young children to provide for. We are happy to state that, in answer to these applications, subscriptions were received amounting to £937 11s., after deducting expenses, postage, &c., of £16 11s. 1d. Of the balance £435 was expended in the purchase of 4 per cent Stock of the Queensland Government, and £473 15s. in the purchase of Guaranteed 5 per cent Preference Stock of the Scottish Australian Investment Company, which will bring in an income of £35 per annum. The Stock was purchased in the names of Major C. D. Davies, John Spiller, and W. Y. Dent, who were appointed Trustees of the Fund for the benefit of the children of the late E. O. Brown, with discretionary powers to expend the sums at their disposal in such a manner as may seem to them most advisable, and to close the account at the expiration of twelve years from October 20th, 1886, the date of the Trust Deed, by which time the youngest child would be 18 years of age. The widow has received a grant of £100 from the War Office, and a gratuity of £50 from the Royal Society.

## MEETINGS FOR THE WEEK.

Monday, 23rd.—Society of Arts, 8. (Cantor Lectures). "The Chemistry of Substances taking part in Putrefaction and Antisepsis," by J. M. Thomson, F.C.S.
Tuesday 24th.—Institution of Civil Engineers, 8.
—— Royal Institution, 3. "The Modern Physiology of the Brain, and its Relation to the Mind," by Prof. Victor Horsley, F.R.S.
—— Society of Arts, 8. "The Importance of the Applied Arts and their Relation to Common Life," by Walter Crane.
Wednesday, 25th.—Geological, 8.
Thursday, 26th.—Royal, 4 30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "The Chemistry of the Organic World," by Prof. Dewar, F.R.S.
—— Telegraph Engineers, 8.
Friday, 27th.—Royal Institution, 9. "Etiology of Scarlet Fever,' by Edward E. Klein, M.D., F.R.S.
—— Quekett Club, 8.
—— Society of Arts, 8. "Indian Tea," by J. Berry White.
Saturday, 28th.—Royal Institution, 3. "Victorian Literature," by Prof. John W. Hales, M.A.
—— Physical, 3. "Note on Transformers for Electric Distribution," by Prof. S .P. Thompson, D.Sc. "On Magnetic Torsion of Iron Wires," by Mr. Shelford Bidwell, F.R.S. "On a Strain in a Beam fixed at Both Ends," by Prof. W. E. Ayrton, F.R.S., and Prof. J. Perry, F.R.S.

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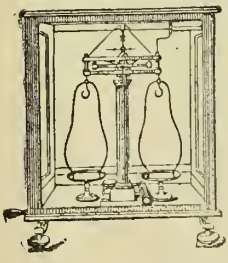

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THE CHEMICAL NEWS.

Vol. LV. No. 1435.

## NOTES ON THE THYMOL AND MENTHOL SUGAR TESTS.

By DAVID LINDO.

These notes refer to some new sugar reactions described in a former paper. The alcoholic solutions of thymol and menthol employed in these experiments were the same strengths as those used in the former ones.

Five c.c. sugar solution,* 1 in 1000 water, were placed in a small beaker; half a c.c. thymol solution added, then 10 c.c. pure sulphuric acid (sp. gr. at 28° C. 1·813†) after about a minute; added 10 c.c. more sulphuric acid, and after another interval of a minute poured the product into 300 c.c. distilled water. The colour of the mixture was almost a pure magenta. Stirred well and before a precipitate had formed, removed 6 c.c.—equal to rather less than 0·0001 grm. of the sugar employed—and diluted this with 96 c.c. water. The pink colour was quite distinct, thus showing the presence of one part of sugar in a liitle more than one million parts of liquid. The volume under observation must, however, be borne in mind. No colour could be seen in a few c.c. of the fluid separated from the mass. The colour faded after two or three hours.

The precipitate having formed in the balance of the original liquid, it was filtered. The filtrate was free from colour, but the washings soon began to pass slightly tinged pink. The precipitate—of a very fine colour—was dissolved on the filter in a little alcohol, and the yellowish solution that resulted mixed with 25 c.c. water and 1 c.c. sulphuric acid. The purple colour was restored, but quickly destroyed on boiling, a small quantity of tarry matter separating.

The solution reacted persistently with sulphuric acid alone, giving a pink colour, which was no deeper when thymol was used with sulphuric acid to test it. The same results were obtained with a precipitate from a menthol product treated in a similar manner. Kingzett and Hake failed to obtain sugar from a camphor precipitate, operating, it would appear, on a much larger scale.

All such experiments, however, can be of little value unless tried on the precipitates in a state of purity. As they are not crystalline, but seem to be of a resinous character, there appears little prospect at present of obtaining them in a pure condition, or at least of being able to discriminate between a pure product and a mixture; otherwise heating in sealed tubes with dilute acid would be worth trying.

As menthol gives no reaction with nitrates or nitrites that could possibly be mistaken for sugar, it is in this respect—but only in this—more reliable than thymol as a test for sugars, or other carbohydrates that react like sugars. In the presence of nitrates or nitrites, however, in notable quantity, sugar cannot be detected by either of these reagents. As regards thymol this is not solely due to the confusion that results from both sugars and nitrates, &c., giving a purple-red colour with the test, but also to the fact that when nitrates, &c., are present in sufficient quantity, the sugar reaction either does not occur or the product is almost immediately destroyed, so that on diluting with water no characteristic colour will be obtained.

An aqueous solution of potassium nitrate, 1·8723 grms. in 100 c.c., was chiefly employed in these experiments, 1 c.c. = 0·010 grm. $N_2O_5$. When the $N_2O_5$ was equal in weight to the sugar present, pale pinks were sometimes obtained on dilution, not permanent, therefore not characteristic of sugar. With 2 parts $N_2O_5$ to 1 of sugar a greenish opalescence was observed; on dilution no trace of pink.

The same results were obtained with the same proportion of $N_2O_5$ to sugar, whether the sugar solution was 1 sugar in 400 water or 1 in 1600 water.

With 4 sugar to 1 $N_2O_5$ very fine pinks were obtained on dilution, permanent, and giving the same kind of precipitate which a weak solution of pure sugar always yields to the test (sugar 1 in 1600).

With menthol the sugar reaction was quite too obscure to be of any value, with equal parts of $N_2O_5$ and sugar the colour being ruddy brown whether the sugar solution was 1 in 400 water or 1 in 1600.

As the proportion of $N_2O_5$ is increased, the colour approaches yellow.

With 4 sugar to 1 $N_2O_5$ very good reds were obtained, but the colour not quite so pure as when $N_2O_5$ was absent (sugar 1 in 1600).

As 2 drops of thymol or menthol solution and 1 c.c. sulphuric acid give the same colour reactions, differing only in intensity with 0·5 c.c. sugar solution,—whether the latter is pretty strong or extremely dilute,—it would seem large excess of these reagents (especially sulphuric acid and thymol) does no harm. Large excess of sugar, however, as might be anticipated, is decidedly injurious.

Using of course 2 drops thymol or menthol solution and 1 c.c. sulphuric acid to 0·5 c.c. sugar solution, if the latter contains 2 per cent sugar no colour will be obtained by either test that can be recognised as derived from sugar after the mixture has stood a few seconds. On diluting the thymol a brown precipitate falls, and menthol soon changes to the same colour.

With 1 per cent sugar solution thymol gives a ruddy brown precipitate on dilution, not characteristic, and menthol soon acquires the same tint. Half per cent sugar solution, however, gives very fine reds with menthol, deep but permanent, differences in depth of colour—as in all cases—depending to a certain extent on variations in the temperature.

If alkaline chlorides or HCl have any influence in marring the delicacy of the tests, such experiments as I have made fail to show it.

Half a c.c. sugar solution, 1 in 40,000, gave as distinct a reaction with thymol when common salt to the extent of 400 times the weight of sugar was present as when it was absent; and deeper reds were obtained by diluting thymol products with pure strong HCl than by diluting with the same volume of water.

Half a c.c. sugar solution, 1 in 20,000, gave as good a reaction with menthol, in the presence of NaCl to the extent of 200 times the weight of sugar, as when the salt was absent.

These experiments have been repeated, but not carried further. The results indicate pretty clearly that HCl or alkaline chlorides may be present in very large proportion without injuring the delicacy of the tests.

If a thymol product diluted with water is mixed with alkali in excess, the colour changes to yellow.

Strong HCl cannot be successfully substituted for sulphuric acid in these experiments. The acid employed to test this contained 30·30 per cent HCl. Using even 2 c.c. in place of 1 c.c. sulphuric acid with half c.c. sugar solution, no colour could be obtained at ordinary temperatures, with either thymol or menthol, using so strong a sugar solution as 1 per cent. On heating, the colour with menthol was not pure red, but yellowish red, the same with sugar 1 in 1000 water; at this dilution the colour was faint.

With thymol there was no difficulty in getting reds down to 1 sugar in 5000 water, but the colour was always weak and dingy.

Falmouth, Jamaica, B.W.I.,
April 25, 1887.

* Cane sugar was used in all the experiments.
† The same acid used in all the experiments.

## GRIQUALANDITE, A PSEUDOMORPH OF CROCIDOLITE.

By G. GRANT HEPBURN, University College, Dundee.

This mineral, which was recently received from a resident in Port Elizabeth, occurs in large quantities on a farm in Griqualand West, South Africa, and appears to be a pseudomorph after crocidolite, which it resembles exactly in structure. Its composition, however, is different from ordinary crocidolite, as it contains no soda, and has practically the whole of its iron in the ferric instead of in the ferrous condition.

It occurs as opaque, asbestos-like fibres, which are non-elastic and of a snuff or golden brown colour. These fibres are arranged perpendicularly between two thin layers, one of galena, and the other of a very dense and extremely hard substance, consisting chiefly of silica, iron, and magnesia. The mineral is in places penetrated by very fine veins of galena.

It has a specific gravity of 3·136, and in hardness lies between 4 and 5, but is very nearly 4. The streak is the same colour as the mineral, viz., golden brown.

When powdered and heated to 120° C. it changes colour from brown to dark red. On cooling, the dark red gives place to a bright red, which is permanent. A splinter of the mineral heated strongly before the blowpipe is infusible, but becomes magnetic and assumes a logwood-red colour.

An analysis gave the following results, from which it appears that it has the composition of a ferric silicate, having the formula, $6SiO_2 \cdot 4Fe_2O_3 \cdot 5H_2O$:—

| | Found. | Calculated for $16SiO_2 \cdot 4Fe_2O_3 \cdot 5H_2O$. |
|---|---|---|
| $SiO_2$ .. .. .. | 56·75 | 56·80 |
| $Fe_2O_3$ .. .. .. | 37·64 | 37·87 |
| $H_2O$ (combined) .. | 4·96 | 5·33 |
| FeO .. .. .. .. | 1·09 | — |
| MgO .. .. .. | 0·10 | — |
| $H_2O$ (moisture) .. | 0·27 | — |
| | 100·81 | 100·00 |

The combined water is a little too high, otherwise it would correspond exactly to the formula $H_2O \cdot Fe_2O_3 \cdot 4SiO_2$, which is that of an acid ferric silicate, thus:—

$$4H_2SiO_3 = H_8Si_4O_{12}$$

$$Fe_2^{iv}H_2Si_4O_{12} = H_2O \cdot Fe_2O_3 \cdot 4SiO_2.$$

Wibel (*Berichte der Deut. Chem. Ges.*, vi., 185) gives the analysis of a mineral having a very similar composition.

In the following table the properties of crocidolite are placed side by side with those of griqualandite:—

| Griqualandite. | Crocidolite. |
|---|---|
| Specific gravity = 3·136. | Specific gravity = 3·2 to 3·265. |
| Colour and streak, golden brown. | Colour and streak, lavender blue to leek green. |
| Non-elastic. | Somewhat elastic. |
| Infusible. | Melts easily to a somewhat frosty glass. |
| Borax bead, brown. | Borax bead, green. |

Determination of the Water in Crystalline Boric Acid.—E. Hintz and H. Gilbert.—The author puts 1·5 grm. commercial caustic lime in a platinum capsule, ignites before the blast until the weight is constant, pours on the lime about 10 c.c. of water, stirs 2 grms. boric acid into the milk of lime with a glass rod, washes the matter adhering to the rod into the capsule, and evaporates on the water-bath to dryness. It is then heated at first with a small flame, then with a full one, and lastly, in order to expel any carbonic acid, for five minutes before the blast. The loss of weight represents water, and in Tuscan samples water *plus* ammonia.—*Zeit. Anal. Chem.*

## AN INTERNATIONAL HYDROMETER.

By FRANK SPENCE.

The idea that the specific gravity of a solution and its strength, or proportion of dissolved constituent, are equivalent things, is a popular fallacy. This is evident from the following facts:—

| Relative proportions of Sulphate of Alumina dissolved in a given volume of water. | Corresponding indications by specific gravity Hydrometer (Water = 1·00). |
|---|---|
| 10 | 1·05 |
| 20 | 1·10 |
| 30 | 1·15 |

Thus, in the column of proportions of substance dissolved, the last figure is three times the first; whereas, in the corresponding column of specific gravities, the last figure is only one-tenth more than the first.

It follows that a workman using a specific gravity hydrometer to ascertain the strength of the liquids with which he is operating, would be entirely misled by its indications. Hence has arisen the necessity for hydrometers directly indicating strengths.

But a perfect hydrometer should show not only the strength of solutions, but their gravity as compared with that of water—the universal standard—or, in other words, their "specific gravity."

Baumé's, Cartier's, and Beck's strength-hydrometers have all arbitrary and artificial scales, and their figures cannot be reduced to the corresponding specific gravity ones without the use of tables. Baumé's, for example, is based upon the highly abnormal indications shown by solutions of common salt.

Twaddell's hydrometer has a normal scale, and a uniform though distant relationship to specific gravity, his figures being reducible to the corresponding specific gravity ones by multiplying them by 5, adding 1000, and placing a decimal point on the right of the left-hand figure. On account of this remote relationship to specific gravity, Twaddell's hydrometer cannot be proposed to French and German chemists as a standard for unifying the scales of different countries.

The International Hydrometer indicates at once both the strength and the specific gravity, and is based upon the very simple principle of subtracting from the specific gravity scale the figure 1·00 for the constant—water—and leaving the remaining proportional figures on the instrument to indicate to the workman the regularly increasing or decreasing strength. The instruction, printed on each instrument, "For specific gravity add 1·00 (Water)," likewise enables the director of an establishment to perceive, in an instant, what is the specific gravity, should he require to know it, or to compare it with any other specific gravity figures.

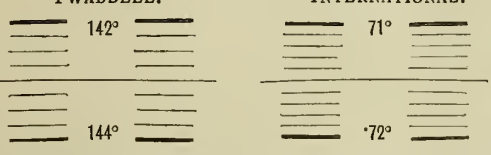
For liquids lighter than water the converse arrangement is adopted; the figures on the scale showing the workman the progressively increasing degrees of "lightening" instead of "weightening," or, in other words, the progressively increasing proportion of "lightening" substance present. At the same time, the words on the instrument "For spec. grav. deduct from 1·00 (water)," enable the chemist, in a moment, to ascertain the specific gravity of the liquid.

The advantages resulting from the unification of the heat-measuring scales of all nations are now universally recognised, and every advanced chemical and metallurgical establishment, at home and abroad, has adopted the French Centigrade thermometer. The desirability, if not necessity, of unifying the discordant scales for measuring the strength of liquids, is equally obvious to the scientific manufacturer, and this object is now proposed to be accomplished by a scale which indicates at once both the strength and the specific gravity.

No. 1 hydrometer covers the range from 1·00 (water) up to and inclusive of 0·10 additional sp. gr. No. 2 covers

the range from 0·10 up to and including 0·20 additional, and so on. Similarly, with liquids lighter than water, No. -1 hydrometer covers the range of figures up to and including 0·10 lighter than water; No. -2, the range from 0·10 lighter up to and including 0·20 lighter, and so on. Thus, any manager or foreman requiring a hydrometer to test a liquid of supposed strength, knows in a moment which No. of instrument to send for; whereas, with Twaddell's and other hydrometers, probably not one person in fifty using them could tell off-hand what range the different Nos. of instruments cover.

Another practical advantage possessed by the instrument is the facility with which the eye can read off its indications—all the strengths shown by the three figures of Twaddell's scale being indicated by two figures on the stem of the International Hydrometer, thus:—




N.B.—It should be borne in mind that the solutions of few if any substances give, throughout, strength-hydrometer indications corresponding *exactly* with the proportions of dissolved constituent. New combinations of the solvent with the dissolved substance, forming at different strengths, or other causes, produce, at these strengths, expansion or contraction of the liquid and consequent aberrations in the scale. Strength-hydrometers are, however, for all practical purposes, regarded as indicators of the regularly increasing or decreasing gradations of strength, which would be shown by the solutions of a perfectly normal substance.

Manchester, May 16, 1887,

## DETECTION AND ESTIMATION OF THALLIUM IN PLATINUM.

By H. N. WARREN, Research Analyst.

Having recently had occasion to heat to redness a number of platinum wires, of different dimensions, I was considerably struck with the intense greenness which several of the wires communicated to the flame of the Bunsen, and at once urged the heat to whiteness by means of a blast burner, and examined it spectroscopically. The light produced consisted exclusively of a single green ray, and was unmistakably characteristic of the metal thallium.

Of the wires submitted to analysis the thinner ones gave by far the most intense flame, apparently owing to the heat being better able to effect the softening of the metal. Samples of platinum foil were also subjected to similar tests, and in the majority of cases they gave a slight green colouration to the flame, although in some cases there seemed apparently a total absence.

I next submitted samples of the same wires to a careful gravimetric analysis, taking 10 grms. of each sample, and dissolving the same in pure aqua regia; after evaporating to dryness on a water-bath the dry residue was redissolved in a small quantity of distilled water, and slightly acidified with pure nitric acid; a few drops of hydriodic acid were next introduced, in order to precipitate the thallium as thallic iodide. The small precipitate obtained was digested for several hours over the water-bath, filtered, and well washed with pure alcohol to remove any free iodine that might contaminate the precipitate. The washed precipitate was then detached from the paper by means of a small quantity of alcohol, and received in a weighed platinum dish, which was afterwards dried at 100° C. until the weight remained constant, and the percentage of thallium present calculated from the weight obtained. This, in more than one case, although trifling, amounted to 0·1 per cent, and averaging from 0·02 to 0·1 per cent, the samples of wire containing by far the largest quantity in comparison with those of the foil.

A similar investigation was performed with several samples of platinum ore, in all of which distinct traces of thallium were obtainable.

Experiments were also performed as regards the action of thallium when alloyed with platinum. The result was that 0·5 per cent rendered the platinum absolutely useless for manufacturing wire from, rendering it decidedly brittle; and even 0·1 per cent considerably impaired its tensile strength and durability, whereas 2 per cent only induced the metal to fuse readily at a red heat.

## THE INFLUENCE OF NITRATE OF SODA ON GUN-COTTON.

By F. NETTLEFOLD, F.C.S.

The hygroscopic effect of nitrate of soda in gunpowder making is also felt in making gun-cotton charges. And since this substance alone does not appear to have the property to the same effect, the following experiments were made with a view to show the reason of the anomaly.

Gun-cotton primers were made $1\frac{1}{4} \times \frac{7}{8}$ in. with 30 per cent nitre—

1. With lime in small quantity, as required by the Government, and 30 per cent $KNO_3$.
2. With lime and 30 per cent $NaNO_3$.
3. No lime and 30 per cent $NaNO_3$.

It being suggested that lime might act as a carrier of water, by conversion to nitrate, reacting under the influence of water.

The experiments were conducted in three series—

1. In the open air in a damp place for 200 hours.
2. " " " 170 "
3. In a closed damp vessel for .. .. 100 "

*Increase in Weight and Water Absorbed, Per cent of Original Weight taken.*

Series I.

| No. of hours. | No. 1. | No. 2. | No. 3. |
|---|---|---|---|
| 12 .. .. .. .. | −0·55 | + 1·4 | + 1·25 |
| 36 .. .. .. .. | −0·66 | + 3·17 | + 2·20 |
| 70 .. .. .. .. | +1·78 | + 2·31 | + 2·40 |
| 120 .. .. .. .. | +1·22 | + 7·99 | + 8·08 |
| 195 .. .. .. .. | +8·4 | +21·40 | +15·30 |
| Loss or gain on the dry charge at end of expt. | −8·5 | + 2·3 | 1·9 |
| Water contained at end of experiment .. .. | 7·92 | | |

The noticeable point in this table is that the potash charges decrease in weight at first, owing to the decomposition and efflorescence of nitre being more rapid than the weight of water absorbed.

The increase in dry weight of the soda primers cannot be accounted for.

Series II.

| No. of hours. | No. 1. | No. 2. | No. 3. |
|---|---|---|---|
| 20 .. .. .. .. | 0 | + 1·98 | + 1·98 |
| 50 .. .. .. .. | −0·15 | + 2·30 | + 2·42 |
| 100 .. .. .. .. | +3·03 | +11·30 | +11·12 |
| 173 .. .. .. .. | +3·10 | +22·30 | +22·15 |
| Loss or gain on the dry charge at end of expt. | −3·46 | + 0·01 | + 0·15 |
| Water contained at end of experiment .. .. | 6·83 | 22·42 | 22·3 |

SERIES III.

| No. of hours. | No. 1. | No. 2 | No. 3. |
|---|---|---|---|
| 24 .. .. .. .. | +0·1 | 4·8 | 4·04 |
| 98 .. .. .. .. | +0·2 | 13·91 | 15·4 |
| Loss or gain on the dry charge at end of expt. | −4·4 | + 0·4 | + 1·3 |
| Water conta ned at end of experiment .. .. | +4·9 | +14·0 | + 17·0 |

The hygroscopic property of sodic nitrate is here clearly seen in all three cases to be greater than potassic nitrate.

The following figures tend to show what changes take place in the gun-cotton, under conditions which approximate to natural atmospheric conditions, usually found in damp mines:—

SERIES I.

*No.* 1.

| | Before Expt. | After Expt. Calc. on primer. | Calc. on original wt. | Diff. | Change in dry weight. |
|---|---|---|---|---|---|
| $KNO_3$.. .. | 31·3 | 28·7 | 26·26 | −5·04 | −8·5 |
| Soluble salts | 31·4 | 31·40 | 29·73 | −1·67 | |
| $KNO_2$.. .. | — | 0·35 | — | +0·35 | |
| Gun-cotton | 66·75 | 65·30 | 59·75 | −7·67 | |
| Alkali $K_2CO_3$ | — | 1·7 | 1·55 | +1·70 | |

(For a loss of gun-cotton of 7·67 there is a corresponding loss of nitre of 5. But it would require 4·65 of nitre for complete combustion, and the 0·35 of $KNO_2$ might make up the difference).

*No.* 2.

| | | | | | |
|---|---|---|---|---|---|
| $NaNO_3$ .. | 25·6 | 21·70 | 21·21 | −4·49 | +2·3 |
| Soluble salts | — | 23·4 | 22·87 | — | |
| Gun-cotton | 72 8 | 74·37 | 72·70 | −0·10 | |
| $NaNO_2$ .. | — | 0·26 | 0·26 | +0·26 | |
| $Na_2CO_3$ .. | — | 0·11 | 0·11 | +0·11 | |

(The nitrate of soda has a tendency to effloresce from the surface of the primers more than the nitrate of potash; hence the loss, while the gun-cotton does not vary much).

SERIES II.

*No.* 1.

| | | | | | |
|---|---|---|---|---|---|
| $KNO_3$.. .. | 31·3 | 31·4 | 30·31 | −0·99 | −3·46 |
| Soluble salts | 31·65 | 32·0 | 30·89 | −0·76 | |
| Gun-cotton | 66·75 | 65·37 | 63·11 | −3·64 | |

(3·64 per cent gun-cotton would require for complete combustion 2·2 per cent $KNO_3$. But as the soluble salts do not increase, it probably decomposed with a lower proportion).

*No.* 2.

| | | | | | |
|---|---|---|---|---|---|
| $NaNO_3$ .. | 25·6 | 21·6 | 21·6 | −4·0 | 0·01 |
| Gun-cotton | 72·83 | 72·0 | 72·0 | −0·83 | |

(Here the sodic nitrate is alone altered).

SERIES III.

*No.* 1.

| | | | | | |
|---|---|---|---|---|---|
| $KNO_3$.. .. | 31·3 | 32·42 | 30·99 | −0·31 | −4·4 |
| Soluble salts | 31·65 | 33·73 | 32·23 | +0·58 | |
| Gun-cotton | 66·75 | 62·94 | 60·17 | −6·58 | |

(Similarly to No. 2, Series I., the loss of gun-cotton has taken place without a sufficiency of nitre and the increase of alkalies).

*No.* 2.

| | | | | | |
|---|---|---|---|---|---|
| $NaNO_3$ .. | 25·6 | 21·31 | 21·4 | −4·2 | +0·4 |
| Soluble salts | 24·26 | — | — | — | |
| Gun-cotton | 72·83 | 73·2 | 72·9 | — | |
| $Na_2CO_3$ .. | — | 0·23 | 0·23 | +0·23 | |

It is noticeable that the nitrate of soda is lost to about 4 per cent without oxidising a relative amount of gun-cotton, and in the potash charges that there is a loss which is apparently accounted for in the above figures by destruction of gun-cotton.

## QUALITATIVE DETERMINATION OF SULPHITES IN PRESENCE OF HYPOSULPHITES AND SULPHATES.

By M. A. VILLIERS.

On treating a solution of a neutral alkaline sulphite with barium chloride, we obtain, by double decomposition, insoluble neutral barium sulphite and an alkaline chloride, and the liquid, which was strongly alkaline at first, becomes exactly neutral to litmus.

If we treat a solution of an alkaline bisulphite with barium chloride, there is still formed neutral barium sulphite, and half the sulphurous acid remains in solution.

Hence it results that if we treat with chloride of barium a mixture of an alkaline sulphite and bisulphite, a mixture which has a distinctly alkaline reaction, even when the proportion of neutral sulphite is small, the solution becomes acid after the addition of the barium chloride, and contains free sulphurous acid.

Upon these facts may be founded an expeditious and convenient process for the detection of sulphites in presence of hyposulphites, which, like the sulphites, evolve sulphurous acid by the action of acids. It is sufficient to neutralise the solution of the mixed salts with hydrochloric acid, if the mixture is alkaline, carefully avoiding any excess of acid, and to precipitate then with barium chloride. The liquid which becomes acid and contains sulphurous acid is then distilled. The sulphurous acid passes over in the first portions of the distillate, and may be recognised. The filtrate may further be treated with iodised potassium iodide and examined for sulphuric acid. The same process is applicable in presence of salts of the thionic series, which evolve sulphurous acid by the action of acids.— *Comptes Rendus*, vol. civ., p. 1177.

## LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1887.

By WILLIAM CROOKES, F.R.S.,

WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Professor of Chemistry at the University of Oxford.

and C. MEYMOTT TIDY, M.B., F.C.S., Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

*To* THE WATER EXAMINER, *Metropolis Water Act*, 1871.

London, May 5th, 1887.

SIR,—We submit herewith the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the same and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

In the supply to the Metropolis for the past month, the proportion of organic matter present in the water has continued uniformly low; though not, indeed, so remarkedly low as in the previous month's supply. Thus, the maximum proportion of organic carbon in any sample

of Thames-derived water was 0·179 part in 100,000 parts of the water; with a mean of 0·162 part in the entire series of samples, as against a mean of 0·172 part for the previous three months' supply.

One only of the Thames-derived samples had to be recorded as otherwise than clear and bright; but several samples of the East London Company's water, drawn from a stand-pipe in the Commercial Road, were found to be "very slightly turbid" from the presence of finely-suspended mineral matter, apparently detached from the lining deposit of the mains in that neighbourhood by exceptional flushings to which they had been subjected. The maximum proportion of organic carbon found in this Company's supply was 0·147 part in 100,000 parts of the water.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

## IN MEMORIAM.

One of the most brilliant luminaries of French science has latterly disappeared from our view. On the eleventh of the present month Boussingault—next to M. Chevreul the *doyen* of the Academy of Sciences—closed his long and honourable career, and at the advanced age of 85 has gone to his rest.

We first hear of him in the scientific world as far back as 1821, when, at the age of nineteen, whilst a student at the Mining School of St. Etienne, he published a memoir on the compounds of platinum and silicon.

Shortly afterwards he was appointed by the Spanish government to a professorship at the Mining School of Bogota, and accordingly set out for South America. Here he threw himself with ardour into his new duties, but on the outbreak of the revolt which ultimately deprived Spain of all her domains on the American continent, he allowed himself to be led away, joined the insurgents, and became attached to the staff of Bolivar. After the war was at an end he became superintendent of the mines of Colombia. In his various capacities he traversed the regions of Venezuela, New Grenada, and Bolivia, and displayed a wonderful activity. Amidst all the distractions of his military and official duties he carried on researches in physiography, chemistry, mineralogy, and geology, and acquired the reputation of a not unworthy successor of Humboldt. More than fifty memoirs written during this epoch remain to attest his zeal for science.

On his return to France he was appointed to a chair at the Conservatoire of Arts and Manufactures in 1837. In 1837 he became a member of the Academy of Sciences, a member of the National Society of Agriculture in 1842, whilst in 1844 he was appointed a member of the Council of Hygiene.

His attention seems to have been drawn to agricultural chemistry in consequence of his marriage with Mlle. Le Bel, the sister of an eminent agriculturist. In conjunction with his brother-in-law he began on the estate of Bechelbronn those series of experiments which have since rendered this name classical. It may fairly be said—as was admitted at the Congress of Moeckern—that he was the creator of agricultural stations and of the system of continuous experimentation on a practical scale to determine the best conditions of the growth of crops. He afterwards continued his experiments at Liebfrauenberg, a domain on the slopes of the Vosges where he completed a number of the most important researches on the atmosphere and the soil, on the gaseous exchanges between the air and the plant during the fixation of carbon, and on nitrification. In the midst of these experiments he still continually reverted to his former studies, to geology, metallurgy, and terrestrial physics.

Sanitary questions occupied a great and latterly an increasing share of his energies. He studied the influence of poisonous matters upon miners and manufacturers, and busied himself with means for their protection. More than thirty years ago he drew the attention of the authorities to the dangerous character of the waters drawn from wells for the supply of Paris. He was also concerned in improving the sewers of Paris and with the utilisation of sewage and of all animal refuse.

On the occasion of his funeral, on the 14th inst., the customary discourses were pronounced by M. Schlœsing, on behalf of the Academy of Sciences, and by M. Troost, as representative of the Council of Public Health.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, May 19th, 1887.*

Mr. William Crookes, F.R.S., President, in the Chair.

Messrs. S. F. Benford, Edgar Hall, J. S. Jackson, and Hugh Gordon were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Bott, Ph.D., Owens College, Manchester; William Nathaniel Evans, 66, Stackpole Road, Bristol; Khasberao B. Jadhara, Baroda, Bombay Presidency, India; J. M. Kavanagh, Victoria Mill, Herbert River, North Queensland; John T. Sheard, Gas Offices, Bloom Street, Salford; Henry Livingstone Sulman, 13, Brewster Gardens, St. Quintin Park, W.; Frederick Percy Watson, 31, Carholme Road, Lincoln.

The following papers were read:—

46. "*The Formation of Hyponitrites.*" By Professor Dunstan and T. S. Dymond.

Zorn (*Ber.*, xv., 1258) has stated that alkali nitrites and nitrates are readily acted on by ferrous hydroxide, forming hyponitrite, ammonia, nitrogen, and nitrous oxide. Divers and Haga (*Trans.*, 1884, 87, and 1885, 364) allege that alkali nitrites yield much ammonia, but neither hyponitrite nor hydroxylamine, nor any gaseous product; and that alkali nitrates are wholly unaffected: while nitric oxide in presence of alkali is to a large extent converted into ammonia by ferrous hydroxide, but yields no hyponitrite.

The authors find that nitric oxide in the absence of alkali is reduced by ferrous hydroxide to nitrous oxide and nitrogen; no ammonia or hyponitrite is formed. In the presence of an alkali (sodium hydroxide) nitric oxide is partly reduced to nitrous oxide and nitrogen, and partly absorbed: the solution contains hyponitrite and ammonia, but on standing with excess of ferrous hydroxide it evolves nitrogen, and the hyponitrite disappears. The amount of hyponitrite formed depends within certain limits on the quantity of alkali which is present, on the quantity of ferrous hydroxide used, and on the time during which action is allowed to proceed. When three formula weights of ferrous hydroxide, $Fe(OH)_2$, and one of nitric oxide are used, the quantity of hyponitrite formed increases with each formula weight of sodium hydroxide that is added. About 20 per cent of the nitric oxide may be converted into sodium hyponitrite.

Alkali nitrites and ferrous hydroxide readily interact, producing nitrogen, nitrous oxide, ammonia, and hyponitrite. The amounts which are formed of these substances depend on the quantity of ferrous hydroxide used, and also on the time during which the action continues. Excess of ferrous hydroxide after some time converts sodium nitrite entirely into nitrogen and ammonia. As a lecture experiment, it is recommended to dissolve 5 grms.

of ferrous sulphate in about 25 c.c. of water, and to precipitate the liquid with sufficient of a 10 per cent potash or soda solution to leave the mixture faintly alkaline; 1 grm. of sodium nitrite dissolved in about 25 c.c. of water is then added, and the mixture stirred. After effervescence has ceased, and the liquid has stood for about half an hour, it is filtered. If the filtrate is diluted with an equal volume of water, and carefully neutralised with acetic acid, on the addition of silver nitrate a pale yellow precipitate of silver hyponitrite (mixed with some silver nitrite) will be obtained. Or a few drops of a silver nitrate solution may be added to the liquid before neutralisation; but in this case the precipitate will rapidly darken in colour. Alkali nitrates are hardly at all affected by ferrous hydroxide; small quantities are slowly converted into ammonia.

In explaining their results, the authors draw attention to the simultaneous formation of hyponitrite and hydroxylamine when sodium amalgam acts on dissolved sodium nitrite. They show that the ammonia is not derived from a further action of sodium amalgam on the hyponitrite, which yields only nitrogen. Similarly, ferrous hydroxide liberates nitrogen from sodium hyponitrite, but no ammonia is formed.

They consider that the action of sodium amalgam on a solution of sodium nitrite is best explained by supposing that the sodium nitrite combines with two hydrogen-atoms, forming $NaN(OH)_2$.

This compound may decompose, yielding hyponitrite: $NaN(OH)_2 = NaNO + H_2O$; or it may undergo reduction, yielding hydroxylamine,—

$$NaN(OH)_2 + 2H = NaOH + NH_2OH,$$

and also ammonia and nitrogen,—

$$4NaN(OH)_2 + 10H = 4NaOH + N_2 + 2NH_3 + 4H_2O.$$

Ferrous hydroxide, it is suggested, acts in the same way; being a substance which will combine with the hydroxyl of water when sodium nitrite is present to unite with the hydrogen. Any hydroxylamine which may be formed will at once be converted into ammonia by ferrous hydroxide. The authors find that when excess of ferrous hydroxide is used, and nitrogen and ammonia are the only products, the reaction takes place almost exactly in accordance with the equations—

(i.) $4NaNO_2 + 8OH_2 + 8Fe(OH)_2 = 4NaN(OH)_2 + 8Fe(OH)_3$;

(ii.) $8NaN(OH)_2 + 6OH_2 + 14Fe(OH)_2 = 8NaOH + 3N_2 + 2NH_3 + 14Fe(OH)_3$.

Since nitric oxide in presence of alkali yields exactly the same products as nitrites, the change can be most readily explained in the same way, assuming that the compound $NaN(OH)_2$ is first formed.

47. "*Ozone from Pure Oxygen.*" By W. A. Shenstone and J. Tudor Cundall.

The authors describe an apparatus in which oxygen has been prepared and stored without the possibility of air gaining admittance. So far as it is possible to determine the purity of the gas by tests, it would appear certain that it has contained at most 1-5000th of nitrogen. The oxygen has been collected and sealed up in glass tubes containing phosphoric oxide, in contact with which it has been kept for periods ranging from eight weeks to eight months. Subsequently it has been submitted to the action of electricity, and the ozone produced has been measured. In one experiment made at 10° C. no less than 11·7 per cent of the oxygen taken was converted into ozone. This is a very considerably higher proportion than has been obtained either by Brodie or by the authors from ordinary oxygen when similar means of electrification are employed, but not so high as was obtained by Andrews and Tait, who, however, worked in a different way, and the exact value of whose results is uncertain in consequence of the tendency of the sulphuric acid that they used in their gauges to absorb ozone.

The action of dry ozone on dry mercury has also been studied. Dry ozone from pure oxygen is decomposed in the well-known manner by pure and dry mercury, but without visible oxidation of the mercury. Further, when a definite volume of oxygen is ozonised and afterwards left in contact with mercury for many hours, the oxygen almost entirely recovers its original volume, the small differences observed between the initial and final volumes being probably due to the difficulty of measuring oxygen with accuracy in a tube partly coated with mercury.

The authors point out that the apparently high yield of ozone obtained under somewhat unfavourable conditions as to temperature may be due—

1. To the absence of nitrogen, the presence of which Andrews has shown is, under some conditions, very unfavourable to the production of ozone.
2. To the character of the electric discharge, which is most free from large sparks when the air and glass surfaces from which the discharge takes place are free from moisture.

The paper concludes with a note on the character of the silent discharge of electricity in ozone generators of the Siemens type, the influence of dryness on the character of the discharge being discussed.

Very full details are given of the method they now employ for preparing and storing pure oxygen. The method might readily be adopted in the case of other gases that do not attack mercury. The apparatus was chiefly constructed for the production of pure gases for various other experiments on the action of electricity on gases that are still incomplete.

48. "*The Volumetric Relations of Ozone and Oxygen.*" A Lecture Experiment. By W. A. Shenstone and J. Tudor Cundall.

Soret and Brodie have shown that if $v$ be the contraction produced on the electrification of a mass of oxygen, then $2v$ will represent the further contraction that will occur on absorbing the ozone formed by means of turpentine. If it be true that ozone completely dissolves in turpentine, this indicates that three measures of oxygen are concerned in the formation of two measures of ozone. The authors describe an apparatus which they have constructed for readily exhibiting Soret's observation to a class.

Discussion.

The President said that he had been accustomed to join tubes *in situ* in the manner described by Mr. Shenstone. He added that it was possible to join together two different kinds of glass by means of a little soft white enamel, such as could be obtained from Powell's.

Mr. Fairley had also joined tubes in the manner described by the authors: calling attention to Brodie's ozonising apparatus, he remarked that the tube used by Brodie was probably thinner than was used by the authors.

Dr. Armstrong thought that the results of the authors' experiments on the action of mercury on ozone were a valuable contribution to our knowledge of the influence of minute amounts of third bodies on the course of chemical change. He suggested that it was important, if possible, to determine the extent to which oxidation took place in presence of varying minute amounts of moisture, in order to ascertain if this exercised an influence comparable with that exhibited in Prof. H. B. Dixon's experiments on the rate of propagation of the explosive wave in a mixture of carbonic oxide and oxygen.

Mr. Shenstone said that experiments such as were suggested by Dr. Armstrong, although very difficult with mercury, might probably be carried out with silver, which effected the decomposition of ozone with extraordinary facility. In reply to the question put by Mr. Page, he was quite unable to account for the peculiar condition assumed by the mercury when submitted to the action of the ozone. He had not been successful in joining tubes with the aid of the enamel spoken of by the President, but, on the other hand, had found it easy to join even

combustion tubing to soft glass by means of an oxy-hydrogen jet.

49. "*On the Thermal Phenomena of Neutralisation and their Bearing on the Nature of Solution and the Theory of Residual Affinity.*" By S. U. Pickering.

In dilute solutions the heat of neutralisation of an alkali is a constant quantity, independent of the nature of the alkali; and the majority of acids give the same results with any given base, whence it follows that M,R,Aq − M',R,Aq = M,R',Aq − M',R',Aq, where M and R are electropositive and electronegative radicles respectively. Each term of this equation is made up of two quantities, M,R (heat of formation of the salt molecule) and MR,Aq (true heat of dissolution of the salt), and it is impossible that such a relationship should exist were these actions independent of each other; they must be part of one quantity, and as M,R is a chemical action, so also is MR,Aq. The affinity of M and R are not entirely saturated by their combination with each other, and it is only by the further combination of the compound with water that saturation becomes complete. The equation can obtain only if the water satisfies the residual affinity of either the non-metallic or the metallic atom, and in the event of atomic valencies being whole numbers all the terms of the equation will be equal, whereas if these valencies are not whole numbers the equation will be made up of two pairs of equal terms.

The recognition of the heat evolved in any action being an absolute measure of the affinities saturated is necessitated by a study of these thermal results.

The few cases in which acids have a higher heat of neutralisation than the majority may be explained by their residual affinity being in excess of that which water can saturate; while in those cases where abnormally low results are obtained the salt is probably partially dissociated by the water.

Owing to the heat of neutralisation being independent of the nature of the base, it follows that the heat of formation in solution of similar salts of two different metals differs by a constant quantity, whatever the non-metallic radicle may be.

Discussion.

With reference to the hypothesis submitted to the Society in 1885, by Mr. Pickering, that the valency of an atom is never a whole number, but slightly smaller or larger, Dr. Armstrong remarked that it was impossible at present to put any such hypothesis to the test, owing to the complexity of the phenomena which had to be interpreted. On the other hand, the hypothesis to which attention had been directed by Helmholtz, in the last Faraday lecture, involved a precise and clear conception —that of a definite unit-valency—and was a necessary deduction from Faraday's law of electrolysis: in the speaker's opinion there was as yet no other course open than to consider the facts in the light of this hypothesis. He was, however, entirely of Mr. Pickering's opinion with regard to the interpretation to be given of the thermal values obtained on neutralising dilute solutions, having already, in fact, as Mr. Pickering had pointed out in his paper, used the same argument in reply to Dr. Nicol in the course of the discussion on the nature of solution at the meeting of the British Association at Birmingham. Dr. Nicol did not appear to have recognised its force, to judge from the remarks at the conclusion of his paper in the current part of the *Transactions*; and disregarding the evidence afforded by the heat-evolution on dissolution of many salts—which can only be due to one cause, viz., to association of the dissolved substance with water—claims, in support of his contention, that hydrates do not exist in solution, the results of the thermal study of changes which it is almost beyond doubt are of a complex character, and which have hitherto remained uninterpreted.

50. "*The Action of Metallic Alkylates on Mixtures of Ethereal Salts and Alcohols.*" By T. Purdie, Ph.D., B.Sc., Professor of Chemistry In the University of St. Andrews.

The author having observed (*Trans.*, 1885, 855) that the ethylic salts of fumaric, cinnamic, and oxalic acids are converted into the corresponding methylic salts by the action of a solution of sodic methylate in methylic alcohol, finds that the reaction in question is of general application: that is to say, when a mixture of an alcohol with an ethereal salt containing a different alcoholic radicle from that of the alcohol, is treated with small quantities of sodic or potassic alkylate, an interchange of radicle takes place between the alcohol and the ethereal salt; and that the chemical change exhibits in a marked degree the character of continuous action. It is supposed that the reaction is effected by the continuous formation and decomposition of a compound of the ethereal salt with the alkylate.

Besides the cases mentioned above, a similar reaction is found to occur when minute quantities of alkylate are added to the following mixtures: methylic oxalate with ethylic alcohol; amylic oxalate with ethylic or methylic alcohol; and ethylic oxalate with amylic alcohol.

Also in the case of mixtures of amylic acetate with ethylic or methylic alcohol; ethylic acetate with amylic alcohol; and phenylic acetate with ethylic alcohol.

A series of blank experiments to which no alkylate was added was performed for purpose of comparison. While the extent of interchange of alcoholic radicle occurring in the latter is usually small, the interchange in the former amounts, under similar conditions, frequently to 50 per cent, and in some instances is almost quantitatively complete.

Discussion.

Dr. Armstrong remarked that, as Prof. Purdie had not failed to point out, the exchange of radicle occurring between the ethereal salt and the alcohol is most probably effected by the alternate production and decomposition of an additive compound formed by the union of the salt with the alkylate, in the manner suggested by him in a "Note on the Action of Sodic Ethylate on Ethylic Oxalate and other Ethereal Salts," communicated to the Society in January, 1874 (*Ber.*, vii., 129). Several applications of the principle involved in this explanation were to be found in the edition of vol. iii. of "Miller's Chemistry," by Mr. Groves and himself (at pp. 861, 907, 923), and the formation of ethylic acetoacetate from ethylic acetate and sodium ethylate was there represented (p. 909) by equations identical with those recently put forward as original by Claisen and Lowman; whose experiments throw as much, but no more, light on the genesis of the aceto-acetate as Geuther's original experiments—a fresh proof that these last are still not rated at their proper value. It was remarkable, also, that it was not generally recognised that sodium ethylate, not sodium, was the effective agent in transforming ethylic salts, W. Wislicenus having, for example, in his recent paper, represented the change effected by sodium in mixtures of ethylic salts as directly due to the sodium, and as involving the formation of sodium substitution-derivatives. The additive compound of the sodium alkylate with the ethereal salt had been represented by himself and others as an atomic compound, the assumption being made that the elements of the alkylate became distributed; it might be pointed out that it was, perhaps, unnecessary to make this assumption, it being conceivable that change would supervene if once the alkylate became associated with the ethereal salt without its elements becoming distributed.

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*Research Fund.*

A meeting of the Research Fund Committee will be held in June. Fellows desiring grants are requested to make application before June 11th.

# NOTICES OF BOOKS

*Handels-Bericht, von Gehe und Co., in Dresden.* (Commercial Report, by Gehe and Co., of Dresden). April, 1887.

This pamphlet contains, as usual, a notice of the present state of the market for drugs and chemicals, accompanied by forecasts of probable fluctuations in value. In the introductory pages we notice the following significant remark:—"The war of all against all which in politics is as yet only threatened is, in the commercial sphere, now for years becoming a more and more striking fact."

The first portion of the work is devoted mainly to pharmaceutical preparations. The classification, however, is by no means very exact. Thus we find, in this section, metallic aluminium, sulphate of ammonia, chloride of lime, salts of strontia, tannin, &c., all of which are used much more extensively in the arts and manufactures than in medicine, and would, we submit, find a more suitable place in the second part of the work. The nomenclature adopted here is also peculiar, and we think objectionable. Chemical compounds are designated not by the names given to them in chemical text-books but by the peculiar Latin epithets applied to them by German physicians and pharmacists. Some of these names are apt to mislead. Thus potassium chlorate figures here as "kalium chloricum," whilst potassium chloride is styled "kalium chloratum."

In the section treating of "chemico-technical products and dye-wares" we find repeated mention of the conventions entered into among manufacturers in various countries to maintain or improve prices by a restriction of production. Thus chloride of lime—or, as it is here called, "calcium hypochlorosum"—has been raised in price from £6 per ton to £8, by an agreement among the chief English producers.

Under many articles, however, we still find complaints of unremunerative prices. Thus alizarine is now in such a state of depression that its manufacture is no longer profitable. Of the aniline colours it is also said that their prices, which previously yielded only a minimum gain to the makers, have fallen still lower during the past six months. It is a suggestive fact that, in view of the low figures offered for the by-products of the gas-manufacture, new methods of utilising the tar are eagerly sought for, and some managers of works are again burning it under the retorts to economise coke.

Artificial indigo is no longer mentioned, but the writers hope that some of the 103 species of indigo-plant found native in Africa may be successfully cultivated in the possessions recently acquired by Germany in Africa, so as to compete with the supply from India. Due note of this threatened competition should be taken by our planters, who may assuredly succeed in improving both the quality and the yield of their produce.

The consumption of the extracts of dye-woods appears to be still increasing, notwithstanding the coal-tar colours.

The cultivation of annatto, formerly restricted to Cayenne, Guadeloupe, and Brazil, seems to have been lately extended to Java and Cochin China.

Cochineal is likely to become still cheaper, since its cultivation, or rather collection, has been taken up in the La Plata territories, where both the insect and its food-plant are abundant, especially in the provinces Cordoba, Mendoza, Santiago, del Estero, and Rioja. In Tucuman it is sold as a paste, in the form of small dry cakes, under the name "grana."

There was a time when the production of cochineal might have been undertaken in Australia, where the cactus is becoming rampant; but at present prices it is out of the question.

The importation of strontium salts into Germany, chiefly from Britain, has increased in spite of the protective duty of 2s. per 100 kilos. It has risen from 5810 metric cwts. in 1885 to 11,534 in 1886.

Under "soda-saltpetre," which is oddly placed among the pharmaceutical products, a rise of prices is pointed out as probable. The stocks in the principal parts of Europe and America have fallen from 460,000 tons in 1884 to 168,000 tons last year; consequently the convention of the South American producers will find an increase of prices perfectly practicable.

The production of sulphate of ammonia, the chief rival of Chili saltpetre as far as agriculture is concerned, seems to have been steadily increasing in the United Kingdom. The yield in 1883 was 75,000 tons, whilst last year it reached 103,000 tons, all of which except about 20,000 tons was exported.

Carbon disulphide, here called "alcohol sulphuris," is protected in Germany by an import duty of 3s. per 100 kilos.

Mention is made of three aluminium bronzes made in Berlin. No. 1, of a golden yellow colour, is composed of 10 parts aluminium and 90 copper. No. 2 resembles a 14-carat gold, and contains 5 parts aluminium and 95 copper; whilst No. 3, which resembles red copper, is a mixture of 2½ per cent aluminium with copper and silicon. All are readily fusible, resist the action of the air, bear polishing, and can be rolled out as thin as it may be required. No. 3 can be used for telegraph-wires in place of silicon bronze.

As a solder for joining aluminium we find recommended an alloy of 5 parts zinc, 2 parts tin, and 1 part lead, melted together and rolled out into thin sheets. The surfaces of aluminium to be soldered must be scraped clean, and then covered with paraffin to prevent oxidation, which would otherwise prevent adhesion.

Many passages in this useful report confirm the utterance of an eminent German paper, that commercial competition is now war to the knife.

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*The Phoma-Disease in Vines occasioned by the Parasitic Fungi* Phoma vitis *and* Phoma Cookei. By Felix von Thümen. (Die Phoma-Krankheit der Wienreben verursacht durch die parasitischen Pibze *Phoma vitis* und *Phoma Cookei*.)

It would almost seem that the more useful and agreeable any plant is to man, the more it is attacked by enemies, animal or vegetable, so that he has a hard—and not always a successful—fight to save even a share of the produce for his own use. Thus wheat has its mildew, its smut, its canker, besides such animal foes as the wire-worm, the corn-weevil, the corn-moth, and the Hessian fly, which has really "landed in force" in these realms; the potato has its dreaded *Pteronospora* and its Colorado beetle; whilst the coffee plantations are ravaged by *Hemileia vastatrix*. But above all other cultivated plants the vine is a victim. In addition to the *Phylloxera*, we learn from the present treatise that it is liable to the attacks of about 350 parasitic fungi!

Among these enemies the two species of *Phoma* named in the title play by no means the smallest part, and they appear at present to be occasioning considerable damage in the vineyards of Austria and Hungary. This has led to their careful examination in the laboratories of the "Imperial Chemico-Physiological Experimental Station for the Vineyards and Orchards," at Klosterneuberg, near Vienna.

Fortunately in this case a means—simple and cheap in the extreme—has been found for overcoming the pest. The stems and branches of the vines are brushed over during the winter season with a 10 per cent solution of ferrous sulphate. This agent destroys the spores both of the *Phoma* and of *Gleosporium ampelophagum*, another enemy of the vine.

*Notes on the Literature of Explosives.* By Ch. E. Munroe. No. XII. 1886.

The theory of explosions is the subject of the principal note in this pamphlet. Since Mr. Threlfall published the results of his investigations in 1866, several scientists have worked on the subject, and although much light has been thrown on the matter by Sir F. Abel, Berthelot, and others, still the explanations offered by the last-named experimenter (*Proc. Nav. Inst.*, x., 206, 1884) did not seem satisfactory to Mr. Threlfall. With a view to deciding some of these points he has begun by examining cases where the explosion could be seen and watched. In order to effect this, small glass bulbs filled with mercuric fulminate were exploded in a tank of water provided with glass windows in the sides. Various experiments were tried and the effects noted by this means; and they are summed up in the conclusions—that the shock of an explosion must be transmitted either by the actual bodily motion of the products of explosion through the surrounding medium, which is thereby set in motion; by an undulatory motion; or by vortex rings. Gunpowder and other slow explosives act principally in the first two manners; but the examination of the conditions of the explosion of fulminates, gun-cotton, and others of a similar violent character, points to the strong probability of the formation of vortex rings as a means of transmitting the shock.

The second point considered in this paper is the action of detonators. Sir F. Abel's experiments in this direction, and the theory he suggested with regard to detonation,—that there might be some synchronism between the vibrations caused in air or ether by the influence of fulminate of mercury, and the natural period of vibration of a gun-cotton molecule,—are fully discussed and commented upon, and reasons are given for the non-acceptance of this theory and the adoption of that of vortex rings.

A short note follows on the two new explosives recently adopted by French and German artillerists, viz., *hellhofite* and *melinite*, both of which produce the most terrific effects when exploded in the neighbourhood of earthworks or masonry. Large sums of money have been expended by the French Government in manufacturing a stock of these shells, but unfortunately for them it has been only recently discovered that *melinite* slowly decomposes on keeping, so it appears probable that the money expended in its production is utterly lost.

Several notes follow on the explosion of Flood Rock, the manufacture of rackarock, the decomposition of potassium chlorate by heat, and others, all of which have already been noticed in the Chemical News.

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*Annual Report of the Proceedings of the Sussex Association for the Improvement of Agriculture.* By Thomas Jamieson, F.I.C. 1886.

In the spring of the year 1884 experiments on pasture land were commenced, the object of these experiments being to obtain "information useful in forming new permanent pasture and in improving old pasture." For this purpose two sites were fixed upon, one having been in permanent pasture from time immemorial, and situated on the Sussex formation known as the "Hastings Beds." The other represented the great clay formation known as the "Weald," was practically undrained, and had never been cultivated.

For the first two years the weather was so abnormally bad that probably most of the seeds were killed; but things have since improved, and the results for 1886 realised the anticipations that were formed. For cleaning old pasture four different methods were tried. The defect in many pastures lying in the abundance of weeds they contain, it was necessary to find whether the weeds could be removed by means of a harrow without hurting the grasses: this treatment alone did but little good, but when accompanied by seed and manure the produce was increased by 50 per cent, but the proportion of weeds did not diminish. When, however, the land was lightly ploughed, and then treated as above, the crop was increased by nearly 90 per cent and the quantity of weeds diminished.

Experiments on drainage were made, but the results do not seem to be at all clear, and that it would be premature to draw any inference is shown by the following statement:—"The crops of 1885 appeared even to be lessened by drainage: this may have been due to the drains drying what was already too dry, or to the injury done to the surface soil in process of forming the drains."

The application of *lime* to pasture land has also received some attention, and the results are entirely *against* the practice of using lime. This conclusion is rather astonishing in view of the very general idea that limeing is always advantageous, but it only emphasizes what we have on previous occasions insisted upon—that haphazard chemical manuring is practically worthless, and as likely to do harm as good. Sussex soil evidently does not need the addition of lime, though in other soils it is undoubtedly necessary.

The greater part of this report is occupied with experiments on grasses, the same as those conducted at Glasterberry, in the North of Scotland, and the results obtained at both stations generally agree.

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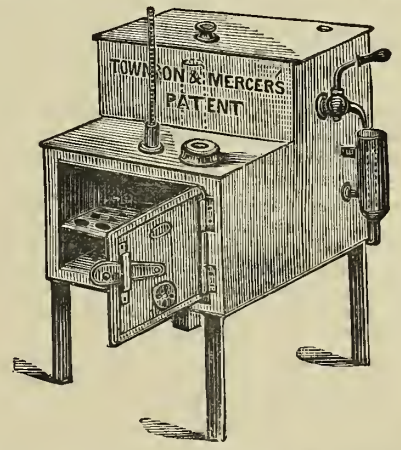
**Hot Water Oven with Cistern.**—Considerable inconvenience is frequently experienced when chemical operations have to be carried on for several hours, necessitating constant attention to keep up the water supply. This difficulty has been effectually overcome by a water oven recently patented by Townson and Mercer, and shown in the accompanying cut, by which arrangement a constant supply of hot water is kept up without lowering the temperature of the oven. The supply cistern, with




a loosely fitting cover, is placed on the top of the oven, into which a tube passes from the oven, which acts partially as a condenser, also to heat the water. The cistern is supplied with a stop-cock from which the heated water drops into the water-level below, and can be so regulated as to just keep up the supply caused by evaporation without any overflow; an automatic supply arrangement is thereby produced for sixteen hours or more, it being simply a question of the size of the supply cistern.

**Reagent for Sulphuretted Hydrogen.**—O. Curtmann.—The author uses an aqueous solution of chloral hydrate mixed with a little ammonia. This reagent gives, even with very small quantities of hydrogen sulphide, a brown colouration on longer standing, the liquid becomes turbid and deposits a brown precipitate. Inversely, a mixture of solution of chloralhydrate and freshly-prepared sulphuretted hydrogen water is a reagent for ammonia.—*Zeitschrift für Analytische Chemie.*

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Zeitschrift für Analytische Chemie.*
Vol. xxv., Part 4.

**A Gas-burner for the Production of Monochromatic Light.**—Noack.—The gas to feed the flame is charged with metallic salts by passing it through a flask in which hydrogen is evolved from zinc and a solution of the metallic salt in question.

**Heating-Apparatus for Determinations of Melting-Points.**—G. Olberg.—The apparatus consists of two vertical glass tubes of the form of test-tubes, connected below by two horizontal tubes melted in. The lower and narrower (1 c.m. in width) horizontal tube is let into the wider vertical tube (3½ c.m. in width and 15 c.m. in height) a little above its bottom, whilst its connection with the narrower vertical tube (2½ c.m. wide and 14 c.m. high) forms its lower end. The upper horizontal tube is wider (2 c.m.), and is fixed into both perpendicular tubes a little below the upper edge. Into the narrower vertical tube the thermometer and the melting-point tube are introduced by means of a cork with two perforations, so that the specimen and the bulb of the thermometer reach nearly down to its bottom. The entire apparatus is filled with a suitable heating tube (oil or the like) so far that the upper connecting tube is about half full, and the wider vertical tube is then gradually heated with a lamp. A circulation is thus produced in the oil in such a manner that it flows from the wider into the narrower vertical tube and returns below. Thus it is effected that in the tube containing the specimen, warmer and warmer strata are constantly sinking down without stirring, and a very gradual elevation of temperature is effected without stirring.

**Boiling Tube for Fractional Distillations.**—R. Hempel.—The inventor combines the two systems of Hempel and Winssinger (see *Zeitschrift Anal. Chemie*, xx., p. 502; and xxiii., p. 199).

**Certain Useful Pieces of Laboratory Apparatus.**—H. Landolt.—These include a combination of a water-bath with a hot water funnel; (2) an apparatus for concentrating very dilute liquids; (3) and a contrivance for sublimation. F. W. Dafert describes, in the *Chemiker Zeitung*, two dialysers and an arrangement to obviate the danger of fire when gas flames strike back.

**A Convenient Double Aspirator.**—A. Gawalowski.—The construction of this apparatus cannot be shown without the accompanying illustration.

**A New Drop Funnel.**—J. Walter.—From the *Journal für Prakt. Chemie.*

**Improvements in Burettes and other Apparatus for Titration.**—A great variety of devices which cannot be here described.

**Applicability of Liquid Paraffin as a Reagent.**—L. Crismer.—This substance dissolves in all proportions in alcohol and ether, if perfectly anhydrous, forming a clear liquid which is rendered turbid by the smallest quantity of water or aqueous alcohol. Absolute alcohol takes up only a certain quantity of paraffin oil, and if brought in contact with a larger quantity of paraffin, two clear liquids separate out, pure paraffin oil and a saturated solution of it in the alcohol. If a small quantity of aqueous alcohol is brought in contact with the latter, an immediate turbidity is produced. If 20 c.c. of chloroform or absolute alcohol are mixed with 0·04 c.c. of a 50 per cent alcohol, and a few drops of paraffin oil are added, a distinct turbidity appears. The author finds, further, that paraffin oil freely dissolves chlorine, iodine, and bromine, as well as colourless phosphorus and its halogen compounds, and those of the alcohol radicles.

**Solid Sulphuric Acid.**—Infusorial earth takes up 3 to 4 parts of sulphuric acid, forming a dry powder which is very serviceable in the exsiccator.

**Method for the Volumetric Determination of Potassa.**—Dubernard.—From the *Journal of the Chemical Society.*

**Calorimetric Determinations of Small Quantities of Manganese.**—M. Osmond.—From the *Bulletin de la Société Chimique de Paris.*

**Application of Neutral Potassium Chromate.**—L. Crismer.—One mol. potassium chromate, 193·96, must liberate 3 atoms iodine, 379·59; consequently, 1 c.c. of the centinormal solution of potassium chromate represents 0·0037959 iodine. Hydrochloric acid sometimes contains traces of chlorine or ferric chloride, which in presence of potassium iodide liberate iodine. Hence the author uses dilute sulphuric acid. If in this reaction a decinormal solution of potassium chromate is used, and the iodine liberated is titrated with sodium hyposulphite in presence of starch, it is very difficult to fix on the end of the reaction. But with the centinormal solution the procees is easy. 20 c.c. of a 10 per cent solution of potassium iodide are acidified with 10 c.c. dilute sulphuric acid (1 : 4) and 20 c.c. centinormal solution of potassium chromate are added. The solution of hyposulphite is then dropped into the iodine solution until the red colour is changed into a clear greenish yellow, 1 c.c. of fresh-prepared starch solution is added, and the operation is completed as usual.

**Method for the Volumetric Determination of Potassium Iodide.**—E. Fallieres.—From the *Journal de Pharm. et Chimie.*

**New Method for the Determination of Sulphur.**—N. von Kloblulow.—This paper will be inserted in full as early as possible.

**New Method of Determining Sulphur in Pyrites.**—J. Clark.—From the *Journal Soc. Chem. Industry.*

**Volumetric Determination of Sulphuric Acid.**—H. Wilsing.—If the liquid to be titrated is acid, and if it contains no compounds precipitable by soda from 20 to 50 c.c. of the solution are mixed, boiling in a porcelain capsule with an excess of a 4 per cent solution of barium chloride (the value of which is previously determined gravimetrically), a few drops of an alcoholic solution of phenol-phthalein (1 : 30) are added, and the boiling liquid is titrated with a 2 per cent solution of soda to incipient reddening. If the solution is acid, phenol phthalein is added to the boiling liquid, and soda solution is added until reddening sets in. The same procedure is used in presence of compounds precipitable by soda. If the solution is alkaline, it is first neutralised with hydrochloric acid.

**Method for Determining Phosphorus in Crude Iron and Steel.**—W. Kallmann.—The author weighs into a platinum crucible from 1 to 10 grms. of the sample, mixes with it from 1 to 2 parts of a mixture of 2 parts calcined magnesia and 1 part potassium sodium carbonate, and ignites over a Bunsen burner for an hour, first in a closed crucible and then in an open one, placed slanting, stirring every ten minutes with a platinum spatula. When cold the pulverulent mass is removed from the crucible into a beaker, and extracted with citric acid with the aid of heat, using so much that the liquid, after warming, has an acid reaction. It is now filtered and washed, first by decantation, and then on the filter with a 1 per cent solution of citric acid, until a specimen of the filtrate no longer occasions, with ammonium chloride and ammonia, a turbidity on standing. The very first portion of the filtrate generally passes through the filter, and must therefore be poured back. The precipitate is easily washed. The filtrate is mixed with ammonium chloride solution to which

one fourth volume of strong ammonia is added, stirring for some time with the glass rod, when the precipitate of ammonium-magnesium phosphate is deposited. It is then allowed to stand until the settlement is complete, when the clear liquid is carefully poured away from the precipitate through a filtrate. The precipitate is dissolved in hydrochloric acid and re-precipitated with ammonia. The double phosphate falls in coarse crystals, and can be filtered off in from half an hour to an hour. The precipitate is then further treated in the ordinary manner and weighed as magnesium pyrophosphate.

**Determination of Phosphorus in Iron.**—J. B. Mackintosh.—From the *Trans. of American Institute of Mining Engineers.*

**Colorimetric Method for the Rapid Determination of Traces of Nitric Acid in Air, Water, &c.**—A. Grandval and H. Lajoux.—From the *Comptes Rendus.*

**A Reaction of Chloral Hydrate.**—Hirschfeld.—If to a solution of chloral hydrate there is added some calcium hydrosulphate, there appears in half a minute a red colour, which finally becomes purple red. A reaction which is fainter, but still distinct, is obtained by adding to a solution of sulphuretted hydrogen, and then lime-water.

**Reactions of Alkaloids.**—A. Luchini.—A table, showing in parallel columns the reactions of the commonest alkaloids with Wenzell's reagent and the author's. The former is a solution of permanganate in 200 parts sulphuric acid, and the latter a solution, prepared hot, of potassium chromate in sulphuric acid. Luchini considers that these reactions together render the other so-called general reactions for alkaloids superfluous.

**Novel Reaction for Digitaline.**—Ph. Lafon.—From the *Comptes Rendus.*

**Characteristic Reaction of Codeine.**—Ph. Lafon.—From the *Comptes Rendus.*

**The Properties of Sparteine.**—A. Houdé.—From the *Journal de Pharm. et Chimie.*

**Determination of Carbon and Hydrogen.**—E. Lippmann and F. Fleisner.—A modification of Kopfer's process, copper oxide asbestos being used instead of platinised asbestos.

**Determination of Nitrogen in Organic Bodies.**—A. von Asbóth finds that the Kjeldahl process may be modified as to be available for the determination of nitrogen in all nitrogenous bodies (including the nitrates) save the pyridin and chinolin group. For substances which, under the ordinary treatment, yield all their nitrogen in the form of ammonia, and which do not give off free nitric acid on treatment with sulphuric acid, the author adds two parts pure cane-sugar to one of the substance. In nitrates and mixtures of such with other nitrogenous matters, the total nitrogen is obtained in the form of ammonia by adding to the substance benzoic acid, 1·7 benzoic acid to 0·5 potassium nitrate being the most suitable proportion.

**Valuation of Crude Calcium Acetate.**—Harcourt Phillips.—From the Chemical News.

**Novel Method of Determining Glycerin.**—W. Fox and J. A. Wanklyn.—From the Chemical News.

**Salicylic Acid in Beer.**—Röse.—The author puts 100 or 50 c.c. in a roomy separating funnel after acidifying with 5 c.c. dilute sulphuric acid, and adds an equal volume of a mixture of equal parts of ether and petroleum ether. He then shakes up the mixture well and distils the filtered ethereal layer into a flask to within a few centimetres. Into the flask, while still hot, there are put 3 to 4 c.c. of water; it is agitated, a few drops of a dilute solution of ferric chloride are added, shaking gently, and the liquid is then filtered through a moist paper. If salicylic acid is absent the filtrate is clear as water, with a faint yellowish tint; if present, the filtrate has the well-known violet colour.

**The Ash of Ceylonese Cinnamon.**—A. Hilger.—In five samples, grown on different soils, the ash was respectively 4·5, 4·8, 3·9, 4·3, and 3·4 per cent; the proportion of soluble matter in the ash ranged from 53 to 88 per cent.

**Analysis of Iron.**—J. Peter.—From the *Bulletin Soc. Chimique.*

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*Bulletin de la Société Chimique de Paris.*
Vol. xlvii., No. 5, March 5, 1887.

**Preparation, Properties, and Constitution of Inosite.**—M. Maquenne.—Inosite melts, without decomposition, at 217°, and boils at 319° in a vacuum. At the ordinary pressure it becomes carbonised before boiling. It is sparingly soluble in cold water, but very soluble in hot water, and insoluble in alcohol and ether. It dissolves readily in hot dilute acetic acid. It is found to possess no rotatory power. Its resistance to hydrogenation, its want of reductive properties, and its non-production of acids on oxidation, prove that it is not an aldehyd. As it does not combine with sodium disulphite, and as it cannot be split up into fatty acids less rich in carbon, it cannot be an acetone. It must, therefore, be a secondary alcohol, an hexa-oxybenzene hexa-hydride.

**Preparation of a Calcium Silico-stannate corresponding to Sphene.**—L. Bourgeois.—The author has obtained this compound as a brilliant white crystalline powder, the particles of which, under the microscope, appear as klino-rhombic prisms.

**Determination of Certain Elevated Points of Fusion and Decomposition.**—H. Le Chatelier.—The author gives his results in the form of tables. The figures which he gives for the fusion-points of the alkaline salts, excepting those of barium, strontium, and calcium chloride, agree well with the determinations of Prof. Carnelley.

**On Kirsch.**—X. Rocques.—Four of the twenty samples examined by the author were genuine kirsch mixed with the inferior brandy known by French spirit merchants as "trois-six," and fourteen were rice-spirit slightly scented with essence of bitter almonds.

**Certain Lecture Experiments.**—A. Mermet.—The author, preparing hypochlorous anhydride by the usual process used, as a refrigerant, liquid methyl chloride instead of a mixture of snow and salt. A violent explosion took place, the apparatus being destroyed and the assistant in charge having the lobe of his right ear torn. This catastrophe is ascribed to the vapours of two liquids coming in contact.

**Two New Colouring-Matters for Wine.**—A. J. Ferreira da Silva.—Already noticed.

**M. Weil's Process for the Volumetric Determination of Grey Zinc Powder.**—Prof. Kupferschlæger.—The author, after briefly describing Weil's process, remarks that zinc powder often contains iron and cadmium which would reduce cupric chloride, as well as does zinc. The author proposes to treat the zinc with sulphuric acid largely diluted with boiling water, to treat this solution with ammonium carbonate, and then to filter. The clear liquid may then be titrated with a normal solution of sodium sulphide. Prof. Kupferschlæger admits that this method determines not merely the metallic zinc present, but also the zinc oxide.

**Agricultural Value of Reverted Phosphate.**—Jules Joffre.—The author maintains that the reverted phosphate is an iron phosphate, and not a bicalcic phosphate. Its agricultural value appears to differ little from that of ground insoluble phosphate, and is decidedly inferior to that of the soluble phosphate.

**Action of Hydrochloric Acid upon the Solubility of the Chlorides.**—R. Engel.—Already noticed.

**Solubility of Magnesium and Calcium Chlorides at 0°.**—R. Engel.—Already noticed.

## MEETINGS FOR THE WEEK.

TUESDAY, 31st.—Royal Institution, 3. "The Modern Physiology of the Brain, and its Relation to the Mind," by Prof. Victor Horsley, F.R.S.
THURSDAY, June 2nd.—Royal Institution, 3. "The Chemistry of the Organic World," by Prof Dewar, F.R.S.
— Chemical, 8. Ballot for the Election of Fellows.
FRIDAY, 3rd.—Royal Institution, 9. "The Application of Photography to Astronomy," by David Gill, LL.D., F.R.S.
SATURDAY, 4th.—Royal Institution, 3. "Victorian Literature," by Prof. John W. Hales, M.A.

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THE CHEMICAL NEWS.

Vol. LV. No. 1436.

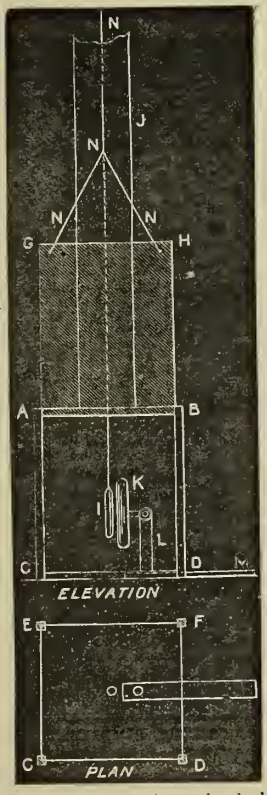
ON THE

# SUPPOSED "NEW FORCE" OF M. J. THORE.*

By WILLIAM CROOKES, F.R.S., Pres. C.S.†

The author commences by quoting the description of some apparatus and experiments which have led M. Thore to suspect the existence of a new force inherent in the human organism. M. Thore suspends a small cylinder of ivory by a fibre of cocoon silk, forming a small pendulum, which hangs freely over the centre of a table. The cylinder having become motionless, M. Thore brings a second cylinder, called the "pillar," about a millimetre from the first cylinder, when the latter begins to rotate clockwise if the pillar is on the left, and counter clockwise if the pillar is on the right of the cylinder. The observer is supposed to face the cylinder and pillar. M. Thore says that the rotation is independent of the nature of the cylinders, of their mass, or the dimensions of the pillar; light, heat, electricity, magnetism, gravity, and air currents, he says, are also inadequate to explain the phenomena.

The author has repeated M. Thore's experiments in apparatus shown in the accompanying figure. It consists




of a glass case, A, B, C, D, E, F, six and a half inches square and seven inches high, with a rising glass window, A, B, G, H, in front and similar windows at the sides. The top is of card, in the centre of which is a small hole. The cylinder, I, is suspended in the middle of the case by a very fine cocoon silk fibre, 5 feet long, surrounded by a card tube, J, attached to the top of the glass box. K is a second cylinder attached to a support, L, M, by a ball and socket joint for convenience of adjustment. The support, M, projects outside the case to admit of the *pillar* being brought close to the *cylinder* and transposed from one side to the other, &c. N is a cord attached to the front glass window, weighted at the end and passing over a pulley for convenience of raising and lowering the glass.

Ivory, ebonite, glass, and metal have been used for the cylinders and for the pillars. The pillars have also been made square, round, and wedge-shaped in section, and the surfaces have been bright and lamp-blacked. The mode of experimentation is the following: — The cylinder being at rest, the observer sits down in front of the apparatus with his face 8 inches from the cylinder and pillar, taking precautions to keep the breath as much as possible away from cylinder and pillar. The pillar is always placed on the right of the cylinder. On raising the front glass the cylinder commences to rotate in the opposite direction to the hands of a clock, the side nearest the observer moving to the right.*

In other experiments a flask of boiling water, a candle, and a hot platinum wire have been used as the source of radiation. The results of more than 50 experiments are given in tables, showing the material of the pillar, the maximum speed of one revolution, the number of revolutions, and the exciting agent. Experiments tried with an ascending current of air of different degrees of intensity in front of the apparatus. prove that air currents are inoperative in producing the action.

The results leave little doubt that the action is one of radiation from the face or other warm body in front of the apparatus, and that there is nothing special in the human organism beyond the heat it radiates to produce rotation of the cylinder.

Radiant heat (and in less degree light) falling on the lampblacked surfaces is absorbed, and increases the surface temperature. There are two ways in which this increase of temperature may act:—

1. It may produce a current of warm air, rising in front of the surfaces of the moving body; to replace this, cold air will come in from all sides, and striking against the delicately suspended cylinder cause it to rotate. If, however, the source of heat is of considerable surface, such as the face or a Winchester quart bottle full of warm water, it is difficult to imagine that there will be much tendency to rotate in one direction rather than in the other.

2. An increased surface temperature of the cylinder and pillar may produce an increase of molecular pressure between the two bodies, and thus give rise to motion, after the manner of the radiometer. In this, as in the former case, the movement should be in the opposite direction to what it is in reality, as it would be produced by mutual repulsion acting between the sides nearest the source of heat.

It seemed likely that information, decisive as regards one or other of these two theories, might be gained by suspending the cylinder in a glass tube attached to a Sprengel pump, and taking observations at different degrees of exhaustion.

In experiments tried by the author in 1875† the noteworthy fact was ascertained, that two bodies of different temperature attracted each other at normal atmospheric pressure; the attraction rose as the pressure diminished, until, at a tension of 1·15 millims., it was nearly four times what it was in dense air. Above this exhaustion the attraction suddenly dropped and changed to repulsion, which at the best vacuum obtained was nearly thirteen times stronger than the attraction in air.

* "Une Nouvelle Force?" Par J. Thore. Dax, 1887.

† Abstract of a Paper read before the Royal Society, May 26, 1887.

* This is called the *negative* direction, and when the rotation is clockwise it is called *positive*.

† *Phil. Trans.*, 1875, Part 2 (pp. 528 to 532).

Two forms of apparatus are described by the author, wherewith experiments were tried during exhaustion, and an exact parallelism was established between the attraction or repulsion of the cylinder by a hot platinum spiral, and the positive or negative rotations of the cylinder under the influence of a warm body brought near.

The two phenomena run absolutely in parallel lines; when there is attraction negative rotation is also produced; when the exhaustion is such that the attraction is *nil*, the rotation is *nil* also; when the attraction changes to repulsion the rotation changes from negative to positive; and when the vacuum is very good, so that the repulsion between the two heated bodies is at its maximum, then also the positive rotation is the strongest. It is impossible to resist the conclusion that the two sets of phenomena are due to the same cause, and that as air currents did not produce the attractions observed in the 1875 experiments, so likewise are they equally inoperative in giving rise to the present rotations of the suspended cylinder.

If the rotation is produced by a reaction between the suspended and fixed body, it follows that were both free to move each would rotate, but in opposite directions. To test this, another apparatus was made, having two delicately suspended cylinders, one millimetre apart, in a glass tube capable of being exhausted. In a table the results of 22 experiments are described, observations having been taken at intervals during exhaustion. Down to 14 millims. pressure the two cylinders rotate negatively (*i.e.*, the right hand cylinder rotates clockwise, and the left hand cylinder counter clockwise). Between 14 and 3 millims. there is no rotation, and below 3 millims. the rotation is positive, the movement at an exhaustion of 0·0495 millim. being five times as strong as it was originally.

The motive force producing these rotations is, at high exhaustions, the molecular impacts between adjacent surfaces of the suspended cylinders excited by the radiation falling on them from the hot water, hot spiral, or a candle (which is equally effective). But what produces the negative rotation at ordinary atmospheric pressure? *Air currents* are the obvious explanation, but there are grave reasons for believing this explanation inadequate. In the first place actual air currents when tried do not produce the desired result. Secondly, it is most logical to assume that as the present set of experiments are strictly parallel with those tried in 1875, and as in each case the results at high exhaustions are due to molecular bombardment, so also must the similar results at low exhaustions be due to the same cause.

Finally, 21 experiments in the form of a table are described, in which an apparatus was employed, specially designed to eliminate the interfering action of air currents, and submit the molecular bombardment theory to crucial experiments. The results are considered by the author as conclusive in favour of this explanation.

Addendum, May 24, 1887.

I sent M. Thore a detailed account of my experiments, asking him to favour me with any comments or remarks he might wish to make. I have just received a long communication, partly printed and part in MS., in which he describes many fresh experiments, and adduces arguments to show that my dynamical explanation is not sufficient to account for more than a few of the facts he describes, and saying that he "persists in still believing that this force emanates from the observer, or else that the observer is the indispensable intermediary for its manifestation."

The experiments are numerous and are devised with great ingenuity. It is impossible in the space of a brief abstract to do more than refer to a few of the principal facts here brought forward. M. Thore commences by objecting to my having experimented in an enclosed space, saying that he always operates in free air. He thinks that enclosure may almost or quite suppress his force. To this I can reply that I myself verified nearly all M. Thore's facts of rotation (including those just now communicated), when working in the free air of a large room, and it was only when I found the delicacy of the observations was impeded by draughts and currents that I put screens round the apparatus. I have not found glass screens interfere materially with any of the rotations. M. Thore now says that it is necessary to hold the pillar or the exciting body in contact with the hand during the whole duration of the experiment. I was not aware that importance was attached to this point, but I have since repeated many of my former observations, holding the pillar in the hand. The results are certainly stronger, but the extra heat imparted to the apparatus is in my opinion sufficient to account for this. M. Thore brings forward many new and ingeniously devised experiments to prove that heat cannot be considered the cause of the movement. He exposes the instrument to the full sun and then brings it into a cool dark room; he suspends it over boiling water; he places a large block of ice between the cylinder and the observer; he similarly interposes metallic vessels full of boiling water between the cylinder and observer (the observer not moving from his place in front), and he tries the experiment in a hot chamber alternately moist and dry, without finding the regularity of the movements interfered with. I have tried most of these, and obtained results corroborating M. Thore's, but I have also tried the experiment of quietly bringing near to the stationary cylinder a bottle of hot water and observing the movement from a safe distance through a telescope, and I find that the hot bottle is able to effect rotation as well as the observer.

Among the curious observations mentioned by M. Thore is this:—Placing the pillar in front of the cylinder (between it and the observer), if the pillar is held with the right hand the movement is clockwise, and if the left hand is used the rotation is counter-clockwise. The right hand is stronger in its effects than the left hand in the proportion of 1 to 2.

M. Thore has given in addition a large number of curious and interesting observations, using two, three, and more movable cylinders and recording their movements under a great variety of circumstances. I admit I do not see at once how all these are to be explained on the molecular bombardment theory. But this theory has not yet explained all the anomalous results I have recorded in my papers on "Repulsion resulting from Radiation," although I believe it capable of doing so; and I therefore think that it is not necessary to call upon a new force to explain any of M. Thore's results which radiation does not yet seem able to account for.

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ON THE

## DISSOCIATION OF SOME GASES BY THE ELECTRIC SPARK.*

By J. J. THOMSON, M.A., F.R.S.,

Fellow of Trinity College, and Cavendish Professor of Experimental Physics in the University of Cambridge.

The gases considered are iodine, bromine, chlorine, and nitrogen tetroxide. The effects of the spark on iodine and bromine were investigated in two ways. In the first method the iodine was placed in a tube from which the air had been exhausted, and which was furnished with a gauge which served to measure the changes of pressure in the tube. The liquid in the manometer was sulphuric acid, and in order to avoid any disturbance due to the absorption of the iodine vapour by this substance, the discharge tube was doubled so that the iodine vapour was symmetrically placed with reference to the sulphuric acid. The system was then placed in an oil-bath and maintained at a temperature which varied in different experiments from about 200° to 230°.

* Abstract of the Bakerian Lecture delivered before the Royal Society, May 26, 1887.

On sparking through such a tube with an induction coil giving a spark about 3 inches long in air, the pressure rapidly increased at first, but the rate of increase gradually diminished and the pressure finally becomes steady. On stopping the coil by far the greater part of this increase is permanent, or at any rate lasts for several hours. It is not due to the decomposition of the vapour from the sulphuric acid in the gauge, for it does not occur if there is no iodine in the gauge, or if the iodine is replaced by bromine. This increase of pressure can be produced by the silent discharge as well as by ordinary sparking. In order to test this point more completely, I had an arrangement made by which, instead of determining the increase of pressure by the sulphuric acid gauge, the vapour density of the iodine after sparking could be measured. In this arrangement the iodine was never near any sulphuric acid.

The result of these determinations is shown in the following table, and it is seen that the results confirm those obtained by the first method.

Unsparked iodine—

| Pressure. | Temperature. | (H = 1). Vapour-density. |
|---|---|---|
| 440 | 215 | 137 |
| 420 | 214 | 130 |
| Sparked iodine— | | |
| 618 | 220 | 110 |
| 420 | 216 | 115 |
| 166 | 214 | 84 |
| 170 | 232 | 86 |

In the last experiment the vapour-density was determined twenty-four hours after the sparking.

These figures point to very considerable dissociation of the iodine; in fact the dissociation produced by the spark at 214° is as much as that produced by Victor Meyer at the temperature 1570° C.

The appearance of the dissociated iodine is not greatly different from that of the unsparked; its colour, however, is, I think, a little lighter and not so uniform. I was not able to detect any change in the absorption spectrum produced by the sparking. The electric strength of the sparked gas was, however, less than that of the unsparked.

*Bromine.*

When the experiment with the pressure gauge is made with bromine instead of iodine, it is found that there is a considerable increase of pressure produced by the passage of the spark, but that this disappears almost as soon as the sparking, and on determining the vapour-density of the sparked and unsparked bromine it is found that they are identical, it seems most probable that the difference between bromine and iodine is not that the bromine is not dissociated by the spark, but that the atoms combine very much more quickly than the iodine atoms. The vapour-density determinations showed that bromine vapour is dissociated if it is heated for a long time at a low pressure, even though the temperature is not very high.

The results of these determinations are given in the following table:—

| Pressure. | Temperature. | Density. | Remarks. |
|---|---|---|---|
| 473 | 111 | 80 | |
| 466 | 106 | 81 | |
| 430 | 101 | 80 | |
| 602 | 116 | 79 | |
| 543 | 89 | 81·7 | In bath for 24 hours. |
| 315·5 | 105 | 73 | |
| 235 | 109 | 77 | *Sparked.* |
| 230 | 100 | 66·5 | In bath for 4 hours. |
| 165 | 90 | 77 | Only a short time in bath. |
| 390 | 111 | 70 | In bath for 7 hours. |

These experiments show that it takes a long time for bromine to reach a state of equilibrium, and that for the experiments on the vapour-density, the gas should be kept for a long time at a constant temperature before the experiments are made.

Experiments on chlorine and nitrogen tetroxide are also described in the paper.

## VITALISING AND DEVITALISING OXYGEN.

In the current number of *The Asclepiad* there is, amongst other valuable articles, a most interesting one by Dr. B. W. Richardson, F.R.S., on the vitalising and devitalising action of oxygen on different animals and under different conditions.

In turning back to the records of some of our earlier experimentalists we find very different opinions expressed as to the action of oxygen on the bodies of men and animals. One observer finds that it acts as an excitant, while another shows evidence to the effect that it is a narcotic and a depressant. Let it be well understood that in all cases ample precautions were taken to keep the chambers in which the animals under experiment were placed free from excess of carbonic acid, and analyses made from time to time proved that this was effected. In spite of these precautions Dr. Richardson suspected that some error had crept in, or that something had been overlooked in the experiments in which oxygen was shown to act as a narcotic. He therefore determined to carry out fresh inquiries in which there could be no possibility of any carbonic acid remaining in the chambers: this was effected by maintaining a continual flow of pure oxygen through the chambers, so as to keep them thoroughly ventilated, the temperature of the gas being kept constant at 60° F.

The results of these experiments showed that freshly-made pure oxygen acted in a different manner as a vitaliser on different animals. Some were apparently unaffected; others were rendered feverish; but in no case was narcotism produced, so long as the supply of oxygen was kept up. A second chamber was constructed large enough to be divided into compartments, so that all the animals could be kept in the same oxygen under exactly the same conditions; but the results found were identical with the former in every respect.

These observations, important as they are in confirming the results of one previous writer, contradict entirely those of another, who nevertheless conducted his inquiry with ample care, as will soon be shown, although he did not find the real causes which led to the results he found. These causes, like so many other important discoveries, were found in the most unexpected manner. With a view to examine his oxygen Dr. Richardson had two reservoirs constructed, one filled with pure oxygen and the other with pure water. After passing through the chamber in which the animals were placed, the gas was collected by displacement in the reservoir of water: in this manner none was lost, except that consumed by the animals. Before being used a second time it was completely dried, and purified from carbonic acid, ammonia, and all appreciable impurities.

During the first passage of this charge of oxygen the same phenomena were produced as in the previous experiments, but on being passed through the chamber a second time a most remarkable change occurred. The animals all became drowsy. The current was quickened, and the gas in the chamber tested, and found to be simply pure oxygen. Still the drowsiness continued. As the experiment proceeded, the drowsiness—which resembled sleep of the quietest character—increased, until at length the startling result was obtained that pure oxygen, after several inhalations, eventually produces death, although no chemical test will show any difference in its composition from that of the freshly-made gas.

The other experiments previously referred to, when examined with this new light thrown upon them, are found to be perfectly correct. The oxygen was certainly kept free from carbonic acid, but, owing to the chamber being closed and not having a draught of fresh oxygen continually circulating, it necessarily came to pass that after a few hours all the gas in the chamber had been inhaled over and over again, with the curious result of devitalising it just described.

The term *devitalising* does not, however, convey the idea of any known modification in the gas; that it is not chemical in the accepted meaning of the word we have the authority of Dr. Richardson for stating; that there is a change is evident, and we can only hope that chemists will take up the matter and endeavour to find whether this change can be detected by chemical means hitherto unknown.

After having devitalised oxygen, attempts to re-vitalise it were made, and it was found that this could be easily effected by electrically charging it from a set of brushes connected with the positive pole of a frictional machine.

After having discovered an effect, the next thing to do is to find out the cause, and in this instance the problem set is a difficult one. Dr. Richardson himself inclines to the opinion that, "during the contact of the oxygen with the blood or the tissues of the animal, some quality of the gas essential to its vitalising power is lost, so that the gas becomes negative in its action." This sounds more like re-stating the fact than finding the cause, and seems hardly sufficient when considered in conjunction with its properties of supporting life in cold-blooded animals, and also supporting flame as vigorously as ever.

However this may be decided we have several examples of the facts repeatedly occurring, such as what is called the clearing of the air by a thunderstorm, which is evidently a re-vitalising of the oyxgen by means of the electric discharge.

In these days, when we are constantly hearing of bodies having had some properties modified, although the chemical tests at our command are not subtle enough to distinguish any difference in composition, we fall back on a general and convenient explanation, and say the anomalies are caused by a re-arrangement of the molecules. How far will this explanation answer the question set by the facts we have recited? The molecules are all present —why will they support life in a cold blooded and not in a warm-blooded animal?

## RESEARCHES ON THE LITHIA MICAS.*

By F. W. CLARKE.

### I. The Lepidolities of Maine.

In the western part of Maine, along a line running southeasterly from the Rangeley Lakes to a point on the seaboard between Brunswick and Portland, there are a series of veins of albitic granite which are noted for their contents in lithia mica and coloured tourmalines. These localities, in the towns of Rumford, Paris, Norway, Hebron, and Auburn, are all within a narrow belt of about forty miles in length; and with them, as a probable part of the same system, may be classed the spodumene locality in the town of Peru. The northernmost of the known localities is that on Black Mountain in Rumford; but a few fragments of inferior green tourmaline have been found about five miles farther north, in Roxbury—a fact which indicates a prolongation of the belt in that direction. Similarly, a southern extension of the belt is suggested in the territory covered by the towns of Pownal, Yarmouth, and Freeport, a region from which a few casual specimens of lepidolite have been reported. The total width of the belt, so far as has been observed, appears to be not much over fifteen miles, although sharp definition of the area is not yet possible.

In general character the several localities are much alike, although in points of minor detail they vary considerably. With the tourmaline and lepidolite, quartz, muscovite, cleavelandite, cassiterite, and amblygonite are always found, together with a wide range of other species which cannot be considered here. Some of the differences are probably due to the fact that certain localities have been more thoroughly opened up than others, and these differences would probably be eliminated by more complete exploration. In other points, however, the variations are notable and characteristic. For convenience we may briefly consider the several localities separately, beginning with the northernmost and proceeding southward in regular order.

*Rumford.**—This locality, discovered in 1878 by Mr. E. M. Bailey, of Andover, Maine, is situated on the northern slope of Black Mountain, at an estimated elevation of about one thousand feet above the valley. The excavation, so far, has been merely superficial. A part of the lepidolite, which is very abundant, is fairly pure, lilac-purple in colour, and finely granular; but the larger portion of the mineral is coarser in structure and thickly sprinkled with small, opaque, red tourmalines. The colour of the latter is very rich and the appearance of the material carrying the associated minerals is strikingly characteristic. It resembles nothing from the other localities of the region. Green tourmaline occurs here but sparingly, while the spodumene is enormously developed, showing faces over a metre in length. At the other lepidolite localities spodumene is one of the scarcer minerals.

*Paris.*—The famous locality known as Mt. Mica has been so thoroughly studied by mineralogists that no detailed account of it is needed here. The lepidolite occurs both in the ordinary, purple, granular form and in broad foliations resembling muscovite. Analyses of it have been published by Berwerth and by Rammelsberg,† which agree fairly well with the results obtained in this laboratory.

*Hebron.*—The deposit at this point, about seven miles south-east of Mt. Mica, has long been well known to collectors. It has only been superficially opened, however, and deserves more systematic exploration. The lepidolite, which is coarsely granular and purple, is especially interesting on account of its yield in cæsia and rubidia, which, after their identification by Johnson and Allen here, were also found in the lepidolite of Rozena. As yet no complete analysis of the Hebron mineral seems to have been published. For the specimens examined in this laboratory I am indebted to the kindness of Professor G. J. Brush.

Associated with the Hebron lepidolite there have been found many specimens of red and green tourmaline, which, while preserving their crystalline form, have undergone an alteration into a softer mineral of an opaque, talcose appearance. Some of the material so derived from tourmaline has been supposed to be lepidolite; and as it was possible that a study of it might have interest, an analysis was made by Mr. R. B. Riggs. The specimen chosen was originally rubellite, and its specific gravity, as determined by Mr. T. M. Chatard, was 2·87. Analysis as follows:—

| | |
|---|---|
| $SiO_2$ | 43·90 |
| $Al_2O_3$ | 38·71 |
| $Fe_2O_3$ | 0·58 |
| FeO | 0·25 |
| MnO | 0·04 |
| CaO | 0·41 |
| MgO | 0·05 |
| $Na_2O$ | 1·05 |
| $K_2O$ | 10·92 |
| $H_2O$ | 4·25 |
| F | none |
| $B_2O_3$ | trace |
| | 100·16 |

These results show clearly that the alteration product is not lepidolite but damourite, a fact which could hardly be altogether unexpected. The material analysed was received from Mr. N. H. Perry, of South Paris, Maine.

*Norway.*—The specimens from this locality were partly collected during a field expedition, and partly received

* Abstract of a Paper to appear in full in a forthcoming *Bulletin of the U.S. Geological Survey.*

* See G. F. Kunz, *Proc. Amer. Assoc.*, 1885.

† See Third Supplement to Dana's "Mineralogy," pp. 78, 79.

from N. H. Perry. The lepidolite was of two varieties; one pale brown and very finely granular, the other much coarser in structure and white. Most of the associated tourmaline has a peculiar dark oily-green tint; and with many of the specimens a rose-red earthy clay was associated. A partial analysis of the latter was published in "Bulletin No. 9 of the U.S. Geological Survey," but a re-analysis seemed to be desirable and was therefore made by Mr. Riggs. The results are subjoined and show that the mineral approaches nearly to cimolite. The difference from the earlier analysis indicates a non-homogeneity of composition. As to the genesis of the clay, nothing can be said with certainty.

| | |
|---|---|
| $SiO_2$ .. .. .. .. .. | 66 86 |
| $Al_2O_3$ .. .. .. .. .. | 22·23 |
| $Fe_2O_3$ .. .. .. .. .. | 0·47 |
| FeO .. .. .. .. .. | 0·18 |
| MnO .. .. .. .. .. | 0·07 |
| CaO .. .. .. .. .. | 0·42 |
| MgO .. .. . .. .. | 0·33 |
| $Li_2O$ .. .. .. .. .. | 0·29 |
| $Na_2O$ .. .. .. .. .. | 0·46 |
| $K_2O$ .. .. .. .. .. | 0·18 |
| $H_2O$ .. .. .. .. .. | 8·26 |
| F .. .. .. .. .. .. | 0·06 |
| | 99·81 |

*Formula*, $Al_2H_4Si_5O_{15}$.

*Auburn.*—In the western part of this town, near the Minot line, there are two localities for lepidolite, less than half a mile apart. The one longest known is small and unimportant, but the other on the farm of G. C. Hatch, has been quite thoroughly developed.* It has yielded many gem tourmalines, mostly of the paler tints, some remarkable apatites, and perhaps the best crystallisations of lepidolite so far known. The latter mineral occurs in the ordinary purplish coarsely granular form and also in extraordinary perfection as a border upon muscovite; the broad plates of the latter being practically encircled by aggregations of small crystals of the lithia mica. Some specimens of this type have also been found at Paris.

As it was hoped that this mode of occurrence of lepidolite might throw some light upon its genesis, three analyses of Auburn material were made by Mr. Riggs: first, of the common granular variety, secondly of the border upon muscovite, and finally of the latter mineral from the centre of the second specimen. The muscovite analysis came out as follows:—

| | | | |
|---|---|---|---|
| $SiO_2$ .. .. | 44·48 | $Na_2O$ .. .. | 2·41 |
| $Al_2O_3$ .. | 35·70 | $K_2O$ .. .. | 9 77 |
| $Fe_2O_3$ .. | 1·09 | $H_2O$ .. .. | 5·50 |
| FeO .. .. | 1·07 | F .. .. .. | 0·72 |
| MnO .. | trace | | 100·84 |
| CaO .. .. | 0·10 | | |
| MgO .. .. | trace | Less oxygen .. | 0·30 |
| $Li_2O$ .. .. | trace | | 100·54 |

About these results there is nothing unusual.

For convenience the analyses of lepidolite, all by Mr. Riggs, may be given in one table. The water in every case was determined directly by means of the Gooch tubulated crucibie, and most of the lithia separations were effected by a new process, lately devised in this laboratory by Dr. F. A. Gooch, and shortly to be published in full. In the Auburn and Norway lepidolites, however, the old phosphate method was used. The fluorine estimations were all by the Berzelian process. In the figures given for $(KRbCs)_2O$, we have actual determinations based upon the amount of chlorine in the mixed chlorides, and not a mere computation as $K_2O$ from the weight of the chloroplatinates. All important estimations were checked in duplicate, and the table of results represents mean values. Seven analyses were made, as follows:—(See Table, next page).

* See G. F. Kunz, *Am. Journ. Science*, III., xxvii., 303.

As regards cæsium and rubidium the Maine lepidolites offer some points of difference. In the Rumford material an ordinary analysis shows neither; but a special examination upon the alkalies from 150 grms. of mineral gave a spectroscopic trace of rubidium. The Paris lepidolite showed traces of both metals, while the material from Hebron, Norway, and Auburn was much richer. On these lepidolites approximate estimations were made, as follows:—

| | Hebron. Granular. | Norway. White. | Auburn. Granular. | Auburn. Border. |
|---|---|---|---|---|
| $K_2O$ .. | 11·44 | 8·82 | 10·51 | 8·03 |
| $Rb_2O$ } .. | 0·77 | 3·73 | 1·29 | 2·44 |
| $Cs_2O$ } .. | | 0·08 | 0·45 | 0·72 |
| | 12·21 | 12·63 | 12·25 | 11·19 |

In these determinations the cæsium was separated as stannic chloride, and the other two metals were computed indirectly from the amount of chlorine in the mixed chlorides. The results have only a comparative value, and no sharp accuracy can be imputed to them. The methods of separation for the three metals are still far too defective.

The foregoing analyses of the Maine lepidolites, covering several distinct types of the mineral from five different localities, indicate a great constancy of composition. The essential indentity of the mineral with that from Rozena and Cornwall is also shown by the several published analyses of the latter, while the lepidolite from Juschakova is slightly different, in that it contains some manganese replacing aluminum, higher fluorine, and a little chlorine. In most of the analyses the water and fluorine appear to vary reciprocally, suggesting the ordinary replacement of the latter element by hydroxyl. With this slight assumption the formula for lepidolite may be written thus:—

$$Al_2LiKF_2Si_3O_9;$$

a formula which has long had general acceptance, but which now rests upon the surer basis of a wider range of analytical data. It corresponds to the following theoretical composition.

| | Calculated. | | Found. | (Riggs). |
|---|---|---|---|---|
| $SiO_2$ .. .. | 49·18 | | 48·80 to | 51·52 |
| $Al_2O_3$ .. .. | 27·87 | | 24·99 | 28·80 |
| $Li_2O$ .. .. | 4·09 | | 3·87 | 4·98 |
| $K_2O$ .. .. | 12·81 | $(NaKRbCs)_2O$ | 12·07 | 13·68 |
| F .. .. .. | 9·84 | $(FH_2O)$ | 6·69 | 8·25 |

Most of the variations are no greater than we should expect to find in material so difficult to secure in absolute purity as lepidolite. The granular structure of that species is peculiarly favourable to the presence of inclusions, as for example of albite, to which probable impurity some of the soda shown by the analyses may be due. The greatest difference is in the case of fluorine; although some of the foreign analyses, notably Rammelsberg's analysis of the Juschakova mineral, contain very nearly the full theoretical amount.

## II. The Iron-Lithia Micas of Cape Ann.

In the granite quarries of Rockport, Massachusetts, near the extremity of Cape Ann, there are occasional felspathic veins which contain the rarer minerals danalite, cyrtolite, fergusonite, and amazon-stone, together with certain remarkable micas. One of the latter, cryophyllite, was described by Cooke in 1867;* who also analysed an associated "lepidomelane," to which Dana afterward gave the name of annite. The vein from which Cooke obtained his material was long ago blasted away or covered up; but other veins of like nature are still accessible, and from one of them the micas examined in this laboratory were obtained. They were collected by the original discoverer of the locality, Mr. W. J. Knowlton, of Boston, and were, to all appearance, identical with the micas described by Cooke. Among the specimens the two types were clearly recognisable; the one a dark greenish-black lithia mica,

* *American Journal of Science*, II., xliii., 217.

*Analyses of Lepidolite.*

| | A. Purple. Rumford. | B. Foliated. Paris. | C. Granular. Hebron. | D. Border. Auburn. | E. Granular. Auburn. | F. White. Norway. | G. Brown. Norway. |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 51·52 | 50·92 | 48·80 | 49·62 | 51·11 | 49·52 | 50·17 |
| $Al_2O_3$ | 25·96 | 24·99 | 28·30 | 27·30 | 25·26 | 28·80 | 25·40 |
| $Fe_2O_3$ | 0·31 | 0·30 | 0·29 | 0·31 | 0·20 | 0·49 | 0·87 |
| FeO | undet. | 0·23 | 0·09 | 0·07 | 0·07 | 0·24 | 0·45 |
| MnO | 0·20 | trace | 0·08 | 0·55 | 0·17 | 0·07 | 0·23 |
| CaO | 0·16 | trace | 0·10 | — | 0·12 | 0·13 | undet. |
| MgO | 0·02 | trace | 0·07 | — | 0·01 | 0·02 | undet. |
| $Li_2O$ | 4·90 | 4·20 | 4·49 | 4·34 | 4·98 | 3·87 | 4·03 |
| $Na_2O$ | 1·06 | 2·11 | 0·74 | 2·17 | 1·43 | 0·13 } | 13·40 |
| $(KRbCs)_2O$ | 11·01 | 11·38 | 12·21 | 11·19 | 12·25 | 12·63 } | |
| $H_2O$ | 0·95 | 1·96 | 1·73 | 1·52 | 0·94 | 1·72 | 2·02 |
| F | 5·80 | 6·29 | 4·96 | 5·45 | 6·57 | 5·18 | 5·05 |
| | 101·89 | 102·38 | 101·86 | 102·52 | 103·11 | 102·71 | 101·62 |
| Less oxygen | 2·44 | 2·64 | 2·02 | 2·29 | 2·76 | 2·18 | 2·13 |
| | 99·45 | 99·74 | 99·84 | 100·23 | 100·35 | 100·53 | 99·49 |

cryophyllite; and the other a black, brilliant lepidomelane. In some specimens the cryophyllite formed a border upon the broad plates of the other mica, precisely as in the association of lepidolite and muscovite at Auburn. The resemblance in this particular was curiously striking; only the Rockport minerals are less conspicuous than those from Maine, since they lack the contrast of colour which gives the latter their beauty.

The cryophyllite varies considerably in outward character, and three well marked types of it were analysed by Mr. Riggs. They may be described as follows:—A. Broad-foliated, brilliant, blackish-green. B. Paler, dull-green, less lustrous, seemingly altered. C. An aggregation of minute six-sided prisms, dark green, almost granular in appearance, resembling some chlorite. Mean results are given.

| | A. | B. | C. | Cooke's Analysis. |
|---|---|---|---|---|
| $SiO_2$ | 51·96 | 51·46 | 52·17 | 51·49 |
| $Al_2O_3$ | 16·89 | 16·22 | 16·39 | 16·77 |
| $Fe_2O_3$ | 2·63 | 2·21 | 4·11 | 1·97 |
| FeO | 6·32 | 7 63 | 5·99 | 7·98 |
| MnO | 0 24 | 0·06 | 0·32 | $Mn_2O_3$ 0·34 |
| CaO | 0·12 | trace | trace | — |
| MgO | 0·03 | 0·17 | trace | 0·76 |
| $Li_2O$ | 4·87 | 4·81 | 4·99 | 4·06 |
| $Na_2O$ | 0·87 | 0·89 | 0·63 | trace |
| $K_2O$ | 10·70 | 10·65 | 10·48 | 13·15 |
| $H_2O$ | 1·31 | 1·12 | 1·46 | — |
| F | 6·78 | 7·44 | 7·02 | $SiF_4$ 3·42 |
| | 102·72 | 102·66 | 103·56 | 99·94 |
| Less oxygen | 2·86 | 3·11 | 2 95 | |
| | 99·86 | 99·55 | 100·61 | |

It will at once be seen that the three samples examined by Mr. Riggs were sensibly identical, and not far in composition from the material analysed by Cooke. In the latter the fluorine amounted to 2·49 per cent, which is only about one-third of the figure found in this laboratory, while the silica, plus that represented in the $SiF_4$, is sensibly higher. The integrity of the species, however, seems to be clear; and it cannot be identified with zinnwaldite. Empirically, as deduced from the new analyses, the formula of cryophyllite may be written—

$$FeH_3K_3Li_4Al_4F_4(SiO_3)_{10};\ \text{or,}\ R'_6Al_2F_2(SiO_3)_5.$$

With the "lepidomelane" or annite, quite unexpected results were obtained. The material analysed by Mr. Riggs was black, brilliant, broadly foliated, and apparently very pure. His figures are given in contrast with those published by Cooke.

| | Riggs. | | Cooke. |
|---|---|---|---|
| $SiO_2$ | 31·96 | | 39·55 |
| $TiO_2$ | 3·42 | | — |
| $Al_2O_3$ | 11·93 | | 16·73 |
| $Fe_2O_3$ | 8·06 | | 12·07 |
| FeO | 30·35 | | 17 48 |
| MnO | 0·21 | $Mn_2O_3$ | 0·60 |
| CaO | 0·23 | | — |
| MgO | 0·05 | | 0·62 |
| $Li_2O$ | trace | | 0·59 |
| $Na_2O$ | 1·54 | | trace |
| $K_2O$ | 8·46 | | 10·66 |
| $H_2O$ | 4·25 | | 1·50 |
| F | trace | $SiF_4$ | 0·62 |
| | 100·46 | | 100·42 |

It is at once evident that two entirely distinct micas are here represented, and the question is raised whether the Rockport granites may not contain a series of complex isomorphous mixtures. Cooke, indeed, pointed out the isomorphism of cryophyllite with his samples of annite, and showed that the lithia and fluorine in the latter were probably due to admixtures of the former. We now see that at least three micas are involved in the problem to be solved, and the difficulty of establishing definite formulæ is enormously increased. For the present, approximate formulæ only can be assigned to these micas, involving several assumptions, and representing probabilities rather than complete interpretations of the facts. If we unite the groups $SiO_2$ and $TiO_2$ in the new annite, and regard the ferric iron as belonging partly with the alumia, and partly as having been derived by oxidation from the ferrous state, we have the following general formulæ for the two analyses.

Annite, Cooke, .. $R'_8Al_4(SiO_4)_5$.
Annite, Riggs, .. $R'_{14}Al_2(SiO_4)_5$.

For the former, the quivalent of $R'_8$ is approximately $K_2H_2Fe''_2$, and for the latter it is $K_2H_4Fe_4$. These values correspond to the following percentage compositions:—

| | Cooke. | Riggs. |
|---|---|---|
| $SiO_2$ | 39·5 | 36·6 |
| $Al_2O_3$ | 26·8 | 12·4 |
| FeO | 18·9 | 35·1 |
| $K_2O$ | 12·4 | 11·5 |
| $H_2O$ | 2·4 | 4·4 |
| | 100·00 | 100·00 |

Attention has already been called to the fact that some specimens of cryophyllite form borders upon plates of annite, precisely as the lepidolite of Auburn is arranged

about nuclei of muscovite. It accordingly becomes quite probable that similar relations connect the two pairs of minerals; and upon these relations the formulæ so far deduced shed some light. In each case we have a mineral with metasilicate ratios implanted upon an orthosilicate; and a derivability of the one from the other is forcibly suggested. Structural analogies also appear; for in each couplet we have evidence of a common type of nucleus, which may be represented thus:—

Lepidolite nucleus, $Al(SiO_3)_3$. Cryophyllite nucleus, $Al_2(SiO_3)_5$.
Muscovite nucleus, $Al(SiO_4)_3$. Annite nucleus, $Al_2(SiO_4)_5$.

The development of complete structural formulæ from these nuclei is rendered difficult by our ignorance of the part which fluorine plays in such compounds. In the ordinary lepidolites it is easy to conceive of it as united with the aluminum in the univalent group $AlF_2$; but in the iron micas and phlogopite a similar representation is unsatisfactory. A different solution of the problem is therefore to be sought, and it may be found by an application of the well-recognised principle that fluorine and hydroxyl can replace each other isomorphously.

If now we start from orthosilicic acid, $Si(OH)_4$, and regard the hydroxyl groups as successively replaceable by atoms of fluorine, we can conceive of a series of acids ranging from $Si(OH)_4$ to $SiF_4$; and with the aid of such a supposition many of the fluoriferous silicates may be rationally explained. For example, the acid $SiF(OH)_2$ may be considered, and its nucleus, $SiFO_3$, a trivalent residue, can be applied to the discussion of the lithia micas. Upon this basis the formulæ for lepidolite and cryophyllite become curiously significant, especially when written in direct comparison with the structures assignable to muscovite and annite respectively. In every case the assumption is made that double salts are to be represented as substitution derivatives of normal salts of similar type, and the results appear as follows:—

Muscovite.

$$Al\begin{cases} SiO_4 \equiv R_3 \\ SiO_4 \equiv Al \\ SiO_4 \equiv Al \end{cases}$$

Annite (Cooke).

$$Al\begin{cases} SiO_4 \equiv R_3 \\ SiO_4 \equiv Al \\ SiO_4 \equiv R_2 \end{cases} \quad Al\begin{cases} SiO_4 \equiv Al \\ SiO_4 \equiv R_3 \end{cases}$$

Annite (Riggs).

$$Al\begin{cases} SiO_4 \equiv R_3 \\ SiO_4 \equiv R_3 \\ SiO_4 \equiv R_2 \end{cases} \quad Al\begin{cases} SiO_4 \equiv R_3 \\ SiO_4 \equiv R_3 \end{cases}$$

Lepidolite.

$$Al\begin{cases} SiFO_3 = R_2 \\ SiO_3 \\ SiFO_3 \end{cases} Al$$

Cryophyllite.

$$Al\begin{cases} SiFO_3 = R_2 \\ SiO_3 - R \\ SiO_3 \end{cases} \quad Al\begin{cases} SiO_3 - R \\ SiFO_3 = R_2 \end{cases}$$

To zinnwaldite, as represented by the published analyses, a probable structure is not easily assignable; and the variations in its composition suggest that the specimens examined have been mixtures of isomorphous compounds. It needs to be thoroughly reinvestigated, not only for itself, but also in its relations to whatever other micas may be associated with it. The matter of association can never, in the study of the micas, be safely neglected.

Although the formulæ herein assigned to annite and cryophyllite are to be regarded merely as trial hypotheses, there can be little doubt that the ratios between the sesquioxides and the silica are correctly given. These ratios are the ratios indicated by the published analyses of phlogopite; with which, therefore, rather than with ordinary lepidomelane, the Rockport micas are chemically to be classed. Zinnwaldite is already so classed by Tschermak and others, and cryophyllite falls easily into the same category. The subjoined formula fairly represents a typical phlogopite.

$$Al\begin{cases} SiFO_3 = Mg \\ SiO_4 \equiv MgH \\ SiO_4 = Mg \end{cases} \quad Al\begin{cases} SiO_4 \equiv MgK \\ SiFO_3 = Mg \end{cases}$$

—*American Journal of Science*, Nov., 1886.

# ON RED AND PURPLE CHLORIDE, BROMIDE, AND IODIDE OF SILVER: ON HELIOCHROMY AND ON THE LATENT PHOTOGRAPHIC IMAGE.*

By M. CAREY LEA, Philadelphia.

## Part I.

In this series of papers it will be my object to show:—

(1.) That chlorine, bromine, and iodine are capable of forming compounds with silver exhibiting varied and beautiful colouration, peach-blossom, rose, purple, and black. That these compounds (except under the influence of light) possess great stability: that they may be obtained by purely chemical means and in the entire absence of light.

(2.) That of these substances the red chloride shows a tendency to the reproduction of colours. It seems not improbable that the material of the infinitesimally thin films obtained by Becquerel, Niepce de St. Victor, Poitevin, and others in their experiments on heliochromy may be the red chloride.

(3.) That these substances, formed by purely chemical means, constitute the actual material of the latent or invisible photographic image, which material may now be obtained in the laboratory without the aid of light and in any desired quantity. They also form part of the visible product resulting from the action of light on the silver haloids.

For more than a generation past, the nature of the latent photographic image, that which forms the basis of development, has been in dispute. Two theories have been maintained. According to the one, the first effect produced by light is simply a physical change, predisposing the elements of the silver haloid to dissociation, so that when a reducing agent is applied the molecules so affected yield more quickly to its influence. According to the other theory, the invisible image is formed of a subsalt (sub-chloride, &c.). Observations which I published many years ago led me strongly to the first-mentioned of these theories. But of late years results have been obtained not easily reconcilable with it. On the other hand, the theory that the latent image is formed of sub-salt is opposed to striking facts. Silver subchloride, for example, is an unstable substance, quickly destroyed by dilute nitric acid. But I have formed a latent image on silver chloride, and after exposing it for five minutes to the action of strong nitric acid (sp. gr. 1·36) have developed the image without difficulty; the same with silver bromide. Evidently these images, which so strongly resisted the action of undiluted acid, could not be formed of simple subchloride and subbromide of silver, substances quickly destroyed by it.

In the desire to find a satisfactory explanation of the nature of the image based on adequate chemical proof, I have devoted nearly three years of laboratory work to this and to closely allied subjects. I am led to the conclusion that neither of the older views is correct. A truer theory seems to be deducible from the result of some experiments which I published in 1885, to the effect that the silver haloids were capable of uniting with certain other substances, much in the same way that alumina forms lakes. When a silver haloid was precipitated in the presence of certain colouring-matters they combined with it, and, though soluble in water, they could not be subsequently washed out. They had formed a somewhat stable compound, although the proportion of colouring-matter was very small in comparison with the haloid,—evidently much too small to represent a stoichiometrical composition.

Now I find that a silver haloid may, in the same way, unite with a certain proportion of its own sub-salt, which

* *Amer. Journ. of Science*, 3rd Series, vol. xxxiii., p. 349.

by this union quite loses its characteristic instability, and forms a compound of great permanence.

Another explanation is possible: the sub-salt may combine with the normal salt, not in the manner above described, but in stoichiometrical proportion, and this compound may be diffused through ordinary silver haloid. I have not been able to find any reaction decisive between these explanations,* but the general behaviour of the substance seems rather to indicate the first-named explanation as the true one. When the red chloride, for example, has been boiled with dilute nitric acid for a few moments to eliminate any uncombined subchloride, the proportion of subchloride left has never exceeded 8 or 9 per cent in over thirty specimens analysed. If we took this to represent a compound in equivalent proportions, we should have to suppose the union of at least twenty equivalents of AgCl with one of $Ag_2Cl$, which is improbable. If we suppose that these coloured substances containing from less than one-half per cent up to eight or nine per cent of $Ag_2Cl$ consist of a compound of one equivalent of subchloride united to a small number of equivalents of normal chloride, mixed mechanically with a large quantity of normal chloride, then it would be improbable that specimens could not be obtained containing a larger proportion of this compound and consequently of $Ag_2Cl$, but, as already said, specimens containing more than 9 per cent after thorough treatment with nitric acid to remove the uncombined subchloride I have never obtained: generally the amount is less.

Even when silver chloride, bromide, or iodide contains as little as one-half of one per cent of sub-salt combined, its properties are greatly changed. It has a strong colouration and its behaviour to light is altered. Even a much less quantity, one inappreciable to analysis, is capable of affecting both the colour and the behaviour to light.

It is one of these latter forms of this substance that constitutes the actual material of the latent photographic image: adequate proof of this will be given in the second part of this paper.

### Red Silver Chloride.

Of the three haloids, the chlorine salt is the most interesting, because of its relations to heliochromy: it is also the most stable of the three compounds and exhibits perhaps a finer variety of colouration, though the bromide and iodide are also obtainable of very beautiful tints. The chloride shows all the warm shades from white to black through the following gradations: white, pale flesh colour, pale pink, rose colour, copper colour, red purple, dark chocolate, black.

These compounds are obtained in an endless variety of ways: by chlorising metallic silver; by acting on normal chloride with reducing agents; by partly reducing silver oxide or silver carbonate by heat and treating with HCl; by forming sub-oxide or a sub-salt of silver and treating with HCl followed by nitric acid; by acting on sub-chloride with nitric acid or an alkaline hypochlorite, &c.; by attacking almost any soluble salt of silver with ferrous, manganous, or chromous oxide, &c., followed by HCl; by reducing silver citrate by hydrogen and treating it with HCl; by treating a soluble silver salt or almost any silver solution with potash or soda and almost any reducing agent, cane-sugar, milk-sugar, glucose, dextrine, aldehyd, alcohol, &c., and supersaturating with HCl; there is no organic easily oxidisable substance that I have tried that has failed to give this reaction. Also almost any salt of silver exposed to light, treated with HCl and then with hot strong nitric acid, yields it. Almost any of these classes represents a long range of reactions, each susceptible of endless variation. In fact, the more the matter is studied, the more extended the range of reactions is found to be that give rise to the formation of this substance. To show how slight an influence will lead to the production of red chloride instead of white: if freshly precipitated argentic oxide is mixed for a few moments with starch or tragacanth paste and is then treated with HCl, the result is, not white, but pink silver chloride. Even raw starch flour mixed with silver oxide will in a few moments cause it to give a pale flesh-coloured chloride with HCl. Boiled starch or tragacanth paste does this more quickly and acts more strongly, even in the cold, and still more if heat is applied.

Although red is probably the most characteristic colour of this substance, so that I have spoken of it above as red chloride, nevertheless this hardly seems a proper name for a substance that is often purple, chocolate, or black, sometimes brown or even ochreous, sometimes lavender or bluish, and is probably capable of assuming every colour of the spectrum. To call it argento-argentic chloride would infer a stoichiometrical composition that, as already mentioned, seems very uncertain, too much so to serve as the basis of the name. Therefore, and as these substances have been hitherto seen only in the impure form in which they are produced by the continued action of light on the normal salts, it might be convenient to call them photosalts, photochloride, photobromide, and photoiodide instead of red or coloured chloride, &c., and thus to avoid the inexactness of applying the term red chloride to a substance exhibiting many other colours.

(To be continued).

* Silver chloride may be dissolved out by hot solutions of sodium or ammonium chloride, but the subchloride is at the same time decomposed. See beyond under head of "Reactions."

## PROCEEDINGS OF SOCIETIES.

### PHYSICAL SOCIETY.

*May 28th*, 1887.

Prof. W. E. Ayrton, Vice-President, in the Chair.

Dr. S. P. Thompson read "*A Note on Transformers for Electric Distribution.*"

In the simple algebraic treatment of the dynamo several assumptions approximately true for well made machines are made use of. The author finds that a similar set of assumptions for transformers greatly simplifies the algebraic theory.

1. The iron, copper, and insulation are assumed good.

2. The reaction of the secondary on the primary (other than that desired) is small. Thus, if the primary be supposed to be supplied with constant mean current or constant mean potential difference, this is not to be altered by the current in the secondary.

3. No magnetic leakage: so that the coefficient of mutual induction is the geometric mean between their coefficients of self induction.

4. The quantities of copper in the primary and secondary are to be equal.

These assumptions are shown to be legitimate, and the ratio of resistances E.M.F.'s, currents, and coefficients of self-induction are expressed in terms of the ratio of the numbers of convolutions, which ratio is represented by

$$p = \frac{S_1}{S_2}.$$

From analogy with the dynamo it is shown that—

$$E_2 = \frac{\omega M}{\sqrt{R_1^2 + \omega L_1^2}} E_1,$$

where $\omega = 2\pi n$, $E_1$ and $E_2$ the E.M.F's of the primary and secondary respectively, and $R_1$ and $L_1$ the resistance and self-induction of the primary coil. If $R_1$ be neglible the above reduces to—

$$E_2 = \frac{\omega M}{\sqrt{\omega^2 L_1^2}} = \frac{E_1}{p} \text{ since } \frac{L_1}{L_2} = p^2 \text{ and } M = \sqrt{L_1 L_2}.$$

The latter part of the paper contains a general investigation of two neighbouring circuits, both having self-induction, and it is shown that the effective resistance of the primary is increased, and the self induction decreased by closing the secondary circuit.

Mr. Kapp said the investigations assumed the co-efficients of induction to be constants, and that the phases of current in primary and secondary were opposite. The former being by no means true, he asked what values were to be taken? and he believes the phases of current are not opposite in ordinary transformers.

Mr. Swinburne protested against the use of formulæ to calculate the inductions, when the required data could be obtained much more accurately from Dr. Hopkinson's curves of Magnetisation of Iron. He also thought the curve of sines did not nearly represent the current curve for ordinary machines.

Mr. Bosanquet thought the effective magnetisation of a transformer would be different to that of a dynamo, for in the former, permanent magnetisation was not utilised.

In reply to Mr. Kapp and Mr. Swinburne, the author pointed out that, as the coefficients of induction enter in both numerator and denominator, it would not matter which set of values were taken if the resistance was small compared with $\omega L$; and that self-induction tends to smooth out irregularities in the current curve.

Prof. Ayrton described a method of regulating a series transformer devised by himself and colleague some two years ago, based on analogy with a compound dynamo. Referring to the variation of L with current, he sketched a curve connecting them, obtained by Mr. Sumpner at the Central Institution, and mentioned that the E.M.F. curve of a Ferranti dynamo is an exact sine curve. He believes problems involving alternating currents would be greatly simplified by using a new set of measurable quantities, such as will render the equations as simple as possible.

At Prof. Thompson's request Prof. Ayrton exhibited a lecture experiment illustrating the action of transformers. The secondaries of two ordinary induction coils were joined in series through long fine wires, and an incandescent lamp placed in the primary circuit of one, lighted up on completing the primary of the other coil, in which a battery was placed.

"*On Magnetic Torsion of Iron Wires.*" By Shelford Bidwell.

This is an account of experiments made on the twisting produced by sending a current along magnetised iron wires, and the author shows that Wiedemann's explanation of these phenomena (by assuming a difference in molecular friction at the polar and lateral surfaces of magnetised molecules) is unsatisfactory. The wires were magnetised longitudinally by means of a solenoid in the axis of which the wires were suspended. To obtain consistent results it was found necessary to demagnetise the wire between the observations. This is done by reversed currents of gradually decreasing strength, and a simple arrangement of rheostat and commutator devised for this purpose was exhibited.

Two sets of experiments were made, in which the current in wire or solenoid was kept constant, whilst that in the other was varied. The amount of twisting does not increase continuously when the currents are increased, but attains a maximum when the inclination of the helix, representing the direction of magnetisation, is inclined at about 33° to the axis of the wire. When the current in the solenoid was kept constant, and that in the wire increased, permanent deflections remained on stopping the current. For small currents in the wire this deflection was diminished on starting the current, whilst stronger currents increased the deflection. For some intermediate value of the current no change took place, and this value was dependent on the current in the solenoid. Experiments were shown illustrating these phenomena.

## NOTICES OF BOOKS.

*Collection of Lectures on the Natural Sciences.* Edited by Dr. Ernest Huth.—I. *The Periodic Law of the Atomic Weights and the Natural System of the Elements.* By Dr. E. Huth. (Sammlung Naturwissenschaftlicher Vorträge. Das periodische Gesetz der Atom-Gewichte und des naturliche System der Elemente). Berlin: R. Friedländer und Sohn.

Dr. Huth begins his work in a manner consonant neither with historical accuracy nor with ethical justice. He says if we disregard the triads of Döbereiner (1829), "and the less-known studies of Newlands, the merit of having founded (*begründet*) the doctrine of the periodic system of the elements belongs to the Russian chemist Mendeleeff and the German Lothar Meyer." But if we wish to write the history of this great discovery correctly we have no right to disregard the labours of Newlands. That his views—though published in the Chemical News, copied into other Journals, and discussed before the Chemical Society—did not for some time attract the notice which they merited is very true; but is the fact that injustice has been done a fair argument for its continuance? Moreover, there can be no doubt either concerning the conclusions of Mr. Newlands or the dates when they were published, and these show that in "founding" the periodic system—though he did not use the term "periodic"—he has a priority of fully five years as compared with Prof. Mendeleeff. Concerning Prof. Lothar Meyer, it must be remembered that the great Russian chemist does not recognise his claim to any important share in the discovery.

Passing gladly from the historical and necessarily controversial portion, we note with great interest Dr. Huth's "Natural System." He arranges the elements in a double spiral, remarking that, as far back as 1870, Baumhauer proposed to express atomic relations.

It is not easy to give a full explanation of the author's scheme without a graphic representation such as he appends to his memoir. He draws seven radii departing from a common centre. On these he places in succession the numbers of the atomic weights, beginning near the centre with the lowest, at distances in accordance with a determined unit of measurement. The elements on the same radius form a natural family. In the accompanying table he begins with lithium on the first radius at the distance of 3·5 m.m. from the centre as its atomic weight = 7; "then follows glucinum on the next radius at the distance of 4·5 m.m., &c. If this arrangement is followed out quite mechanically, the elements which come upon one common radius,—in this case the second,—Be, Mg, Ca, Sr, Ba, Zn, Cd, and Hg, form a natural family, founded on similarity in their chemical and physical behaviour." On the first radius are found Li, Na, K, Cu, Rb, Ag, Cs, and Au. On the third come B, Al, Sc, Ga, Yt, In, La (accompanied by Ce and Di), and Th. On the fourth we find C, Si, Ti, Ge, Zr, Sn, Tl, and Pb. The fifth radius holds N, P, V, As, Nb, Sb, Ta, Bi, and an undiscovered element X. On the sixth radius follow O, S, Cr, Se, Mo, Te, W, and U. The seventh radius holds F, Cl, Mn (Fe, Ni, and Co very close together), Br, Ru (with Rh and Pd adjacent), I, and Ir, with Pt and Os. The ninth radius is blank.

It will at once strike the reader that in this arrangement hydrogen is wanting. We neither find it indicated in the diagram, nor do we see any explanation of its absence.

In each family—*i. e.*, on each radius—the author recognises a typical element, the one standing nearest the centre and having the lowest atomic weight, and two alternating groups. Thus the first family, monovalent generators of bases, contains the potassium group, K, Rb, and Cs, all electro-positive, forming very powerful bases, decomposing water with violence, and having gradually

increasing specific gravities (0·87—1·52—2), and high gradually-increasing atomic volumes (45·4—56·3—67·5). Their spectra are homologous.

The copper group Co, Ag, Au have also increasing specific gravities (8·9—10·6—19·3), and atomic volumes in which no continuous increase can be traced (7·3—10·18—10·15). Copper and silver have homologous spectra. To this family the author assigns two typical elements, Li and Na.

The author's scheme, as shown in the diagram, requires the construction of a double spiral. One of these spirals is expressed by an unbroken line and the other by a dotted line. So far as the typical elements of each family are concerned these two spirals run together, but afterwards they separate. Thus, on the first radius, K, Rb, and Cs, are arranged on the unbroken line, and Cu, Ag, and Au on the dotted line.

The author's arrangement brings the properties of the elements and their relation to the atomic weights very clearly into view. We cannot perceive that he takes the origin of the elements as absolutely distinct and primordial, or as developed from possibly simpler forms of matter, into consideration.

This little work, however, is well worth the heedful notice of all who feel an interest in the development of the periodic system.

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*Societatum Litteræ.* 1887, No. 1 and 5.

We have no hesitation in pronouncing this new undertaking decidedly useful. Its object is to give each month the titles of the papers read before the Academies and other learned Societies of all nations. No attempt is made to give any idea of the contents of each memoir, which could not, of course, be done at any useful length without rendering the new Journal exceedingly bulky, and consequently expensive.

The sciences taken into account are astronomy, meteorology, physics, chemistry, zoology (for which biology would be a preferable synonym, as it seems to include botany), anthropology, mineralogy, geology, palæontology, and hygiene. Other sciences will be noticed only when bearing directly upon some one of the above-mentioned subjects.

The title is given in Greman, English, and French. We must, however, beg to remind the Editor that the English equivalent for "Naturwissenschaften" is not "Natural History," but "Natural Sciences."

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# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Zeitschrift für Analytische Chemie.*
Vol. xxv., Part 4.

**Phosphoric Acid in Manurial Phosphates.**—E. Aubin.—From the *Moniteur Scientifique.*

**Determination of Indigo in Dyed Woollens.**—Taverne.—The author exhausts a given square surface of the material with chloroform in Soxhlet's extraction apparatus, evaporates the extract to dryness, weighs the residue, dissolves it in sulphuric acid, and determines colorimetrically or by titration with solution of chloride of lime.

**Determination of Resin in Soaps and Fats.**—A. Grittner and J. Szilasi (*Chemiker Zeitung*).—According to the authors the methods of Sutherland, Gottlieb, and Heiner do not give quantitatively useful results. They recommend a modification of Gladding's process. From 1 to 2 grms. soap are dissolved with heat in 80 per cent alcohol, the solution, if acid, is neutralised with ammonia, mixed with excess of a 10 per cent alcoholic solution of calcium nitrate, and filtered when cold. The filtrate passes through at first turbid, and must be repeatedly poured back. The precipitate is washed several times with 80 per cent alcohol, mixed in a roomy flask with an excess of silver nitrate solution, and diluted with three volumes of water. After some shaking the precipitate (if a sufficiency of silver solution has been used) collects on the surface, and the solution is nearly clear. It is filtered and the precipitate is washed with cold water until the washings no longer give a precipitate with hydrochloric acid. The washed precipitate is dried at 70° to 80°, and washed with ether into the same flask in which was the silver precipitate, and which must have been dried internally in the meantime. After some time the ethereal solution is filtered through a dry filter into a graduated 100 c.c. cylinder, and the undissolved portion is washed with ether until the filtrate makes up 90 c.c. The ether which flows through last must be colourless; if 90 c.c. do not suffice, a larger graduated cylinder of about 250 c.c. may be used. The solution is then mixed with about 10 c.c. of dilute hydrochloric acid, well shaken for a long time; the cylinder is then filled with ether or hydrochloric acid up to the mark and shaken again. If the operation has been well managed the precipitate of silver chloride settles quickly, and the ethereal solution of the resin is quite pure and transparent. The volume is read off, from 50 to 60 c.c. are taken with a pipette, the ether is distilled off, the residue dried at 100°, and the resin weighed. From the weight we must deduct 1·6 m.g. for every 10 c.c. of the ethereal solution on account of oleic acid which has been dissolved.

**Examination of Commercial Glycerin.**—L. Sullivan and E. E. Berry.—From the *Analyst.*

**Impurities of Sodium Hydrocarbonate.**—E. Mylius.—This salt sometimes contains thiosulphate.

**Determination of Alkaloids in Belladonna Leaves.**—W. Dunstan and F. Ransom.—From the *Pharm. Journal.*

**Determination of the Cinchona Alkaloids.**—J. E. de Vrij.—From the *Chemist and Druggist.*

**Determination of Urea and of Total Nitrogen in Urine.**—A series of researches made in Pflüger's Institute, for which we must refer to the original.

**A New Form of Ureometer.**—F. Bellamy.—From the *Journal de Pharmacie et de Chimie.*

**Phenylhydrazine as a Reagent for Sugar in Animal Fluids.**—R. v. Jaksch.—Phenylhydrazine can be used for the recognition of sugar in urine, and after removal of albumen in blood and serous liquids. Normal urine yields no phenylglucosazon, but it is regularly obtained from blood, &c.

**Detection of Sugar in Urine by Fermentation.**—M. Einhorn.—Yeast produces fermentation also in urines free from sugar, whence comparative experiments are always needful.

**Reductive Power of Normal Urine.**—M. Flückiger and C. Salkowski.—According to the former author normal human urine has a reductive power equal to that of a 0·15 to 0·25 per cent solution of glucose. Salkowski finds the reductive power of urine higher.

**Quantitative Determination of Glucogen.**—Bruecke.—As sources of error the author points out the possibility of an alteration of the compound by the reagents employed, and also the difficulty of completely extracting it from the tissues under examination.

**Detection of Chloral Hydrate in Animal Fluids.**—Baron H. Tiesenhausen.—The author applies the "shaking out" method used in searching for alkaloids. Absolute ether is the best agent, acetic ether is almost as good, whilst petroleum ether, chloroform, and benzene are not applicable.

Detection of Petroleum in the Animal Body.—W. Jacobson.—The "shaking" method is here recommended. Petroleum ether in the cold takes up mere traces of chloroform, ether, acetic ether, benzene, and chloroform are effectual.

Recognition of Mercury.—T. Lecco.—Metallic mercury, obtained on examining poisoned food for volatile poisons, floated at first as a dark scum upon the colourless distillate. On remaining upon the filter it was converted into metallic globules, recognisable as mercury. Mercuric chloride, which had been mixed with fish and sourkrout after six weeks could not be extracted with alcohol.

Cheese Poison.—Victor C. Vaughan.—The author has isolated from poisonous cheese a ptomaine in acicular crystals. He names it tyrotoxicon. It reduces a mixture of ferric chloride and potassium ferrocyanide, as well as iodic acid, and it is not precipitated by the general reagents for alkaloids.

Studies on the Behaviour of the Ptomaines in Chemico-legal Investigations.—K. Tamba.—This paper will be inserted at length.

Atomic Weight of Cerium.—B. Brauner.—The author finds Ce = 140·2210 (O = 16) or Ce = 139·8707 (O = 15·96). His method of purification was to convert the crude cerium oxides into nitrates, and precipitate the basic nitrate by pouring the concentrated solution of the neutral salts into hot water. By fractionated precipitation in this manner repeated eleven times, he obtained preparations, the purity of which was proved by determining the atomic weight of the metal (or metallic mixture) present.

## MEETINGS FOR THE WEEK.

Monday, 6th.—Society of Chemical Industry, 8. "The Alkaloids—the Present State of Knowledge concerning them, and the Method employed in their Investigation," by Dr. H. E. Armstrong. "Notes of a Recent Visit to some of the Petroleum-Producing Territories of of the United States and Canada," by Boverton Redwood.

Tuesday, 7th.—Royal Institution, 3. "The Hellenism of Alexander's Empire—Macedonia and Greece," by the Rev. J. P. Mahaffy, D.D.

—— Institution of Civil Engineers, 8. (Anniversary).

Wednesday, 8th.—Geological, 8.

—— Microscopical, 8.

Thursday, 9th.—Royal Institution, 3. "The Hellenism of Macedonia's Empire—Egypt," by the Rev. J. P. Mahaffy, D.D.

—— Mathematical, 8.

Friday, 10th.—Royal Institution, 9. "Aquileia, the Precursor of Venice," by Thomas Hodgkin, D.C.L.

—— Astronomica, 8.

—— Quekett Club, 8.

Saturday, 11th.—Royal Institution, 3. "The Helenism of Alexander's Empire," by the Rev. J. P. Mahaffy, D.D.

—— Physical, 3. Exhibition of Puluj Vacuum Tubes, by Dr. Warren de la Rue. "Note on Beams Fixed at Both Ends" and "Note on Magnetic Resistance," by Profs. Ayrton and Perry.

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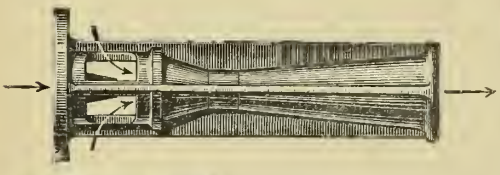

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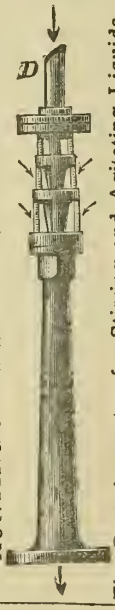

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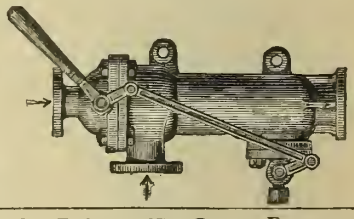

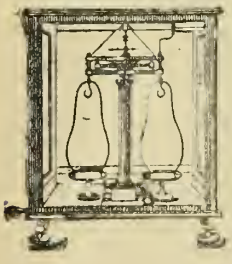

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THE CHEMICAL NEWS.

Vol. LV. No. 1437.

## SILVER SUBOXIDE.

By G. H. BAILEY, D.Sc., Ph.D., The Owens College.

In the number of the *Berichte* recently issued (May 23rd) is a communication from Dr. Otto von der Pfordten, in which he considers "that he has proved with certainty the existence of compounds of suboxide of silver." Having confessed that Wöhler's original method with citric acid is out of the question, he gives two methods of preparation which are in some respects new.

In one of these he adds sodium hydrate solution to neutral tartrate of soda containing some nitrate of silver, and obtains a black powder, "which is at all events the suboxide of silver in combination with an organic acid, probably tartaric," and at the same time there is "probably formed a mixture of organic acids." The powder cannot be filtered; it is decomposed by almost every reagent, and it is purified (*sic*) by washing it by decantation with a solution of sodium sulphate! This tartrate, by the action of caustic alkalies, yields the suboxide which is stable in presence of caustic potash, but, singularly enough, is decomposed by pure water.

Notwithstanding the extreme difficulty, indeed the impossibility, of washing such oxides free from alkalies by decantation, and the importance that in this case every trace of organic matter should be removed, no mention is made of any special precautions in this direction.

In spite of the high degree of probability that metallic silver is contained in the product, and that oxygen is mechanically retained, no criterion (beyond assertion) is given of the homogeneous character of the suboxide.

The interest of the paper centres on an accurate analysis, which to be satisfactory must—for manifest reasons—be made on tolerably large quantities of substance: and yet no details whatever are given of such an analysis, except that a certain volume of a very dilute solution of permanganate of potash was used for the titration. And even if these matters were quite satisfactory the problem is a much more complicated one, for we have in the case in question one or all of the following substances:—

(1) Extremely finely-divided silver
(2) Oxide of silver;
(3) Suboxide of silver.

Each of these retains oxygen, moisture, and alkalies with very great tenacity, and of the behaviour of such physical associations with reagents very little is known. Unless indeed it is possible to prepare, as Wöhler attempted to do, a pure salt of the suboxide of definite composition, the problem is almost incapable of a satisfactory solution. Of course the communication is only given as a preliminary one, but the composition of the suboxide (and any remarks in this note apply equally to the subsulphide) is definitely stated, no lack of details of minor importance are given, and the behaviour with various reagents.

My object is not to criticise the paper, which is indeed more open to criticism in parts not touched upon, but only to point out that the conclusions drawn are not warranted by the evidence.

Atomic Motion.—On Thursday, June 16th, at 8 p.m., Prof. A. W. Williamson, F.R.S., will deliver a Farewell Address to the Chemical and Physical Society in the Chemical Theatre of University College. Subject: "A Few Words on Atomic Motion." Sir Henry E. Roscoe, M.P., has kindly consented to take the chair.

## THE HIGHER OXIDES OF COPPER.*

By THOMAS B. OSBORNE.

*Copper Dioxide.*—When copper hydroxide is treated with hydrogen dioxide at a temperature near 0° C., a brown precipitate is formed, which has been shown to contain nearly twice as much oxygen as copper oxide (CuO), and when acidified yields hydrogen dioxide. When the temperature is somewhat higher a grass-green precipitate is formed, which is sometimes yellow-green or yellow. Krüss (*Berichte*, 2593, 1834) has shown that the brown precipitate, when treated at 0° C. for some days with excess of hydrogen dioxide and frequently shaken, can be filtered, and washed first with alcohol and then with ether, and when entirely freed from water can be dried at 100° C. It then has the composition of $CuO_2$, $H_2O$, or $H_2CuO_3$. When moist, Krüss found that it began to decompose above +6° C. Above this temperature he obtained a grass-green precipitate, which began to decompose above +12° C. He was unable to analyse this latter, as it decomposed readily.

Brodie has shown that if hydrogen dioxide be added to a salt of copper in solution, and then soda, a yellow precipitate is formed.

Krüss obtained a yellow precipitate in too small quantity to analyse, by fusing copper oxide with sodium chloride with access of air. He thought this was a higher oxide of copper and anhydrous, and suggested that it might be the same as Brodie's oxide. Having been unable to find any investigations of the composition of these variously coloured precipitates, I thought it worth while to try and straighten them out. I found that if copper hydroxide (prepared by precipitating nitrate of copper with soda, and washing thoroughly with cold water by decantation, so as to keep the copper hydroxide in a state of the finest possible subdivision) was treated with hydrogen dioxide in small amounts, a green precipitate was formed, which by further action of hydrogen dioxide was changed into a brown. This brown precipitate was yellow by transmitted light, but dark brown by reflected light. When a small amount was shaken up with water it appeared yellow. I found that by mixing increasing amounts of hydrogen dioxide with copper hydroxide the colour of the precipitate varied from a yellow with a greenish tinge through yellow to brown. I made a number of preparations thus varying in colour, and, after washing by decantation free from hydrogen dioxide, determined the hydrogen dioxide set free by dissolving the precipitate, suspended in water, with dilute sulphuric acid. By using a solution of potassium permanganate of known strength the hydrogen dioxide set free was easily determined, the

| | | Per cent. | Weight. | Ratio. |
|---|---|---|---|---|
| I. Grass-green | CuO | 82·35 | 0·6679 | 12·2 |
| | $H_2O$ | 16·29 | 0·1322 | |
| | O | 1·36 | 0·0110 | 1·0 |
| | | 100·00 | | |
| II. Grass-green | CuO | | 0·2717 | 12·7 |
| | O | | 0·00422 | 1·0 |
| III. Yellow-green | CuO | | 0·3040 | 7·5 |
| | O | | 0·00814 | 1·0 |
| IV. Yellower green | CuO | | 0·0701 | 5·14 |
| | O | | 0·00275 | 1·0 |
| V. Yellow (green tinge) | CuO | | 0·4757 | 4·2 |
| | O | | 0·02271 | 1·0 |
| VI. Yellow | CuO | | 0·0633 | 3·1 |
| | O | | 0·00413 | 1·0 |
| VII. Yellow-brown | CuO | | 0·2018 | 1·66 |
| | O | | 0·02457 | 1·0 |
| VIII. Brown (yellow tinge) | CuO | | 0·2847 | 1·48 |
| | O | | 0·03893 | 1·0 |
| IX. Brown | CuO | | 0·2813 | 1·2 |
| | O | | 0·04669 | 1·0 |

* *Amer. Journ. of Science*, Third Series, vol. xxxii., p. 333.

copper in the solution was precipitated with hydrogen sulphide and determined, and the ratio between the excess of oxygen found by titration, and the copper oxide calculated. In this way I found the following ratio between the oxide of copper and the oxygen for the different coloured precipitates, with the exception of I., which was determined by filtering and washing the precipitate with water, alcohol, and ether, cooled to 0° C., drying at 100° C., and then heating in a tube in a current of dry air, weighing the water and copper oxide, and calculating the oxygen by difference.

From these analyses I concluded that the green precipitates were simply mixtures of the yellow with the blue, and that the yellow was a mixture of the brown and the green, the reddish brown colour of the dioxide of copper being complementary to the green, and thus destroying one another and leaving the yellow predominant. That these different colours are mixtures of $CuO_2$, $H_2O$, and $Cu(OH)_2$ was further supported by the fact that I could reproduce any shade of colour by mixing, at any temperature, the brown $CuO_2$, $H_2O$, with $Cu(OH)_2$ in proper proportions Furthermore, the fact that all yielded hydrogen dioxide, when dissolved in dilute acids without evolution of oxygen, is evidence in support of this view.

I found further that I could filter, wash, and dry these precipitates under the same conditions that Krüss employed for $CuO_2$, $H_2O$; and analysis by heating in a tube and weighing the water and copper oxide gave results similar to those obtained by determining the hydrogen dioxide set free by acids, as is seen by I., which was determined in this way, while II. was obtained by the permanganate method. I did not find that any of these precipitates decomposed at low temperatures when free from hydrogen dioxide. Krüss states that the brown precipitates begin to decompose above +6° C., and the green above +12° C. I found that when hydrogen dioxide was present there was a slow evolution of oxygen even below +5° C., which increased as the temperature rose. The precipitate, however, underwent no apparent change until boiled for a moment or two, when it suddenly yielded a large amount of oxygen and black CuO separated out. It would appear, then, that the decomposition below 100° C. is of the hydrogen dioxide, brought about by the action of the copper dioxide.

From the fact that no definite composition can be assigned to any of these various coloured precipitates except the blue copper hydroxide and the brown copper dioxide, that they all yield hydrogen dioxide with acids, that they show the same behaviour on heating, that the different colours can be produced by different amounts of hydrogen dioxide with the same amount of copper hydroxide, and that the colours may be reproduced by mixing the copper hydroxide and the copper dioxide, it seems reasonable to conclude that hydrogen dioxide forms but one higher oxide with copper.

Further, the yellow oxide obtained by Krüss by fusing copper oxide with sodium chloride cannot be the same as Brodie's, as suggested by Krüss, for the latter's compound must have been anhydrous while Brodie's is most probably a mixture of copper hydroxide with copper dioxide. When boiling a small amount of copper dioxide with water I obtained, after a few minutes, a bright yellow precipitate which did not decompose even when boiled for some time, nor on standing some days in a test-tube in the laboratory. There was too little to analyse, and I could not obtain it again. This may have been the same oxide as Krüss obtained by fusing copper oxide with sodium chloride. Lack of time prevented me from further investigating this compound.

*Copper Sesquioxide.*—Crum (*Liebig's Annalen*, lv., 213) described a higher oxide of copper which he obtained by mixing with 1 pound of bleaching-powder, solution sp. gr, 1·06, 50 grains sifted calcium hydroxide, and then adding to the solution, cooled to 0° C., 20 grains of copper oxide dissolved in 70 grains of nitric acid, sp. gr. 1·3. In this way he obtained a blue solution from which a black precipitate separated on standing for some hours. This precipitate evolved oxygen and floated on the top of the solution for some time. After twenty-four hours or more the oxygen ceased to come off, and the precipitate settled to the bottom in a dense condition. This precipitate, when finely divided, had a crimson tinge, and a brighter red colour when rubbed with a rod to a thin layer on glass. When soda was used instead of the suspended lime, he obtained a rose-red precipitate which would not settle. Crum considered the precipitate obtained with lime the same as that obtained with soda, and attributed the difference in colour to a difference in subdivision. He succeeded in washing the dense black precipitate by decanting with cold lime-water, and found that it contained no Cl and an excess of oxygen.

He made several determinations of the ratio between the copper and the oxygen by taking a weighed amount of copper oxide, treating it as described, and measuring the amount of oxygen evolved on acidifying. For 20 grains of copper oxide he obtains in six analyses—I. 1·875, II. 1·886, III. 1·748, IV. 1·915, V. 1·795, VI. 1·747 grains of oxygen. The mean is 1·828 grains. $Cu_2O_3$ would require 1·98 grains. By re-calculating these results, so as to show the ratio between the oxygen found and the copper oxide, I obtained the following numbers :—

| | | | | |
|---|---|---|---|---|
| I. | For 1 atom of oxygen, | | 2·14 | copper oxide. |
| II. | ,, | ,, | 2·15 | ,, |
| III. | ,, | ,, | 2·30 | ,, |
| IV. | ,, | ,, | 2·11 | ,, |
| V. | ,, | ,, | 2·24 | ,, |
| VI. | ,, | ,, | 2·30 | ,, |

From this he concluded that the formula of the oxide was probably $Cu_2O_3$, and further that this oxide acted as an acid and was united with lime, forming a cuprate of calcium, although he obtained no proof that this latter supposition was correct. I repeated Crum's experiments in making this compound of copper with the results as described by him. Hoping to obtain a more accurate determination of the oxygen I tried the following method :—After the precipitate had settled the hypochlorite solution was poured off as far as possible, and then the flask filled up with lime-water and shaken in order to mix thoroughly. After allowing the precipitate to completely settle, 50 c.c. of the clear solution were drawn off and a known amount of ferrous sulphate solution run in, and, after standing some minutes, sulphuric acid added to dissolve the precipitated ferrous and ferric hydroxides, and then the excess of ferrous sulphate titrated off; 50 c.c. of the solution containing the copper precipitate were next drawn from the bottom of the flask and treated with the same amount of ferrous sulphate solution in the same way. The difference in the titre in the two cases represented the oxidation due to the excess of oxygen in the copper compound. The strength of the permanganate solution being known, the weight of oxygen was easily calculated. The first 50 c.c. of clear solution drawn off were in all cases examined for copper, but none was found. The copper in the other 50 c.c. was carefully determined, and the ratio between the copper oxide found and the excess of oxygen calculated. Thus I obtained the following results :—

A.

| | Weight. | Ratio. |
|---|---|---|
| I. | CuO = 0·1888 grm. | CuO = 2·95 |
| | O = 0·0129 ,, | O = 1·00 |
| II. | CuO = 0·1261 ,, | CuO = 3·00 |
| | O = 0·0084 ,, | O = 1·00 |
| III. | CuO = 0·0861 ,, | CuO = 3·25 |
| | O = 0·0053 ,, | O = 1·00 |

B.

| | | Washed thoroughly by decantation. |
|---|---|---|
| I. | CuO = 0·1524 grm. | CuO = 2·38 |
| | O = 0·0129 ,, | O = 1·00 |
| II. | CuO = 0·3182 ,, | CuO = 2·57 |
| | O = 0·0249 ,, | O = 1·00 |

C.

| | | |
|---|---|---|
| I. | CuO = 0·2278 grm. | CuO = 2·83 |
| | O = 0·0162 ,, | O = 1·00 |
| II. | CuO = 0·0716 ,, | CuO = 2·40 |
| | O = 0·0060 ,, | O = 1·00 |
| III. | CuO = 0·1505 ,, | CuO = 2·25 |
| | O = 0·0135 ,, | O = 1·00 |
| IV. | CuO = 0·1217 ,, | CuO = 2·7 |
| | O = 0.0092 ,, | O = 1·00 |

D.

Ferrous chloride was substituted for ferrous sulphate, with results as follows :—

| | Weight. | Ratio. |
|---|---|---|
| I. | CuO = 0·1687 grm. | CuO = 2·93 |
| | O = 0·0117 ,, | O = 1·00 |
| II. | CuO = 0·1614 ,, | CuO = 2·90 |
| | O = 0·0113 ,, | O = 1·00 |
| III. | CuO = 0·0703 ,, | CuO = 2·4 |
| | O = 0·0059 ,, | O = 1·00 |

To what the irregularities in the results were due I am unable to say. The action of the hypochlorite solution on the ferrous sulphate solution was the same when equal quantities were used. No hydrogen dioxide could be found in the acidified solutions, which could act on the iron irregularly and also on the permanganate, and no oxygen escaped on acidifying. I think it probable that a more extended trial of this method would yield satisfactory results.

I tried to use potassium iodide instead of ferrous sulphate, but with little promise of success, as the results varied greatly. I found it exceedingly difficult to obtain constant results with potassium iodide in determining cupric salts alone, except in very dilute solutions, so I abandoned this method as unreliable.

Of course it would be impossible to prove whether calcium was a constituent of this copper precipitate or not when made according to Crum's method, for the suspended calcium hydroxide settles down with the precipitate containing copper, and could not be separated. I found, however, that a large excess of lime-water could be substituted for the suspended calcium hydroxide. By filtering the cold calcium hypochlorite solution carefully into a large flask provided with a rubber stopper, with two holes, through one of which the funnel passed, and through the other a tube filled with broken stick potash to exclude carbonic acid, and then running in about 1 litre of cold lime-water, and adding the copper nitrate solution, the copper hydroxide, which first precipitated, in four or five minutes went into a perfectly clear solution of a deep blue colour. This solution soon changed to a green, and then became nearly black, and from this a precipitate began to separate which had a crimson colour by transmitted light, and appeared exactly like the precipitate obtained with barium hypochlorite instead of calcium, to be described beyond. In a few minutes this precipitate began to evolve oxygen, and was converted into a heavy flocculent black precipitate.

Oxygen continued to be evolved for some hours, and the precipitate was kept floating on the surface. After standing twenty-four hours on ice it had settled. A portion of the solution containing this precipitate was drawn off and washed with lime-water. Under the microscope this precipitate appeared perfectly homogeneous and with a decided pink tint. The oxygen was determined with ferrous sulphate in 50 c.c. of the solution containing the precipitate as before described, and likewise the copper and the calcium. Fifty c.c. of the clear solution were drawn off and found to be free from copper, and the calcium determined. By subtracting the calcium found in the solution from that found in the solution plus the precipitate, the calcium of the precipitate was found. The error due to the amount of the solution displaced by the precipitate was too small to make any serious difference in the results.

In this way I found—

| In sol. + precipitate. | Solution alone. |
|---|---|
| CuO = 0·1869 grm. | None. |
| CaO = 0·1798 ,, | 0·1104 grm. |
| O = 0·0108 ,, | None. |

| | Weight. | Precipitate. Weight. | Ratio. |
|---|---|---|---|
| CaO in p.p. + sol. | 0·1798 | CuO = 0·1869 | = 23·54 |
| CaO in sol. | 0·1104 | CaO = 0·0694 | = 12·39 |
| CaO in p.p. | 0·0694 | O = 0·0108 | = 0·0675 |

The oxygen found in this case is much lower than in the other analyses given, but from the wide variations in the former results its determination cannot be considered more than a qualitative test. The calcium, it will be seen, is in nearly a ratio of two atoms of copper to one of calcium, but I consider this single analysis by no means evidence of anything more than the *presence* of calcium in the compound, and is, so far as I can find, the only direct evidence that copper ever acts as an acid.

The rest of the precipitate from which this sample was taken for analysis was allowed to stand a week packed in ice. It grew gradually more and more dense, and of a brighter pink, until finally it was of a very brilliant rose-red, and formed in places on the sides of the flask very thin layers of a dazzling crimson. In the hope of being able to analyse this as Krüss did the dioxide of copper, I arranged a filter packed in ice and covered with a bell-jar communicating with the air through potash tubes, so as to keep out all carbonic acid, but before I could wash the precipitate it began to turn blue next to the paper. The middle portions were dried in the cold over sulphuric acid and remained quite pink when dry ; but the decomposition had extended so far, I abandoned the analysis, intending to try again, but have not since had time. Unfortunately lack of time prevented me from working further in this direction, and I give my results in hope that they may be of service to others in following up this subject, and settling beyond a doubt the composition of this interesting compound.

When barium hypochlorite in alkaline solutions is allowed to act on copper salts in the cold, a crimson-red precipitate is formed, which somewhat resembles the calcium cuprate just described, but in many respects appears different. But little seems to be known of this compound, it having been supposed to be either a higher oxide of copper, the same as the precipitate obtained with calcium, or else a corresponding barium salt. In hope of being able to analyse this red precipitate, I obtained results which I am entirely unable to account for, and publish them in the hope that someone may be tempted to investigate further and reach a satisfactory conclusion.

In order to make the red precipitate I found it best to put about 50 c.c. of strong baryta water, cooled to about 5° C., in a small flask, add 0·2 grm. of copper as nitrate or chloride, and then to pass chlorine gas through the solution till the colour changed to a blackish green, then to add 100 c.c. of baryta water of 5° C., and after shaking vigorously let stand about half an hour. The precipitate which forms on adding the 100 c.c. of baryta water changes from a blackish green to a dark dirty red, and then slowly to a bright crimson. This precipitate settles very slowly and evolves a gas gradually, and even when kept cold will decompose on standing a few hours. All my attempts to wash it failed utterly. On a filter-paper it decomposed rapidly. When washed with cold baryta water, by decantation, no apparent change beyond the very slow evolution of gas could be seen until several times decanted, when suddenly the crimson colour would disappear and a dirty pinkish precipitate remain. I had to abandon my attempts at decanting more than once or twice, and endeavoured to determine the composition of the precipitate by decanting once, letting the precipitate settle, and then drawing off 50 c.c. of the clear solution

and 50 c.c. of the solution containing the precipitate, and analysing each, the difference representing the precipitate.

No. 1.

| | Precip. + sol. | Sol. | Diff. = p.p. |
|---|---|---|---|
| I. CuO = | 0·2905 | — | = 0·2905 |
| BaO | 0·6965 | 0·6669 | 0·0296 |
| O | 0·0269 | 0·0267 | 0·0002 |
| Cl | 0·0268 | 0·0245 | 0·0023 |
| II. CuO | 0·3422 | — | 0·3422 |
| BaO | 0·7025 | 0·6657 | 0·0368 |

No. 2.

| | | | |
|---|---|---|---|
| I. CuO = | 0·3035 | — | = 0·3035 |
| BaO | 1·0754 | 1·0222 | 0·0532 |
| O | 0·0242 | 0·0240 | 0·0002 |
| II. CuO | 0·3127 | — | 0·3127 |
| BaO | 1·0837 | 1·0197 | 0·0640 |

No. 3.

| | | | |
|---|---|---|---|
| I. CuO = | 0·2603 | — | = 0·2603 |
| BaO | 0·5698 | 0·5577 | 0·0121 |
| O | 0·0082 | 0·0072 | 0·0010 |
| Cl | 0·0142 | 0·0118 | 0·0024 |
| II. CuO | 0·1918 | — | 0·1918 |
| BaO | 0·5627 | 0·5577 | 0·0050 |
| O | 0·0082 | 0·0064 | 0·0018 |

The above analyses show a small amount of barium in the precipitates, compared with the copper, which varies greatly with the different preparations and considerably in the different samples of the same preparation, while duplicate determinations in the solutions agree quite closely. A little chlorine was also present, but it seems more probable that the barium and chlorine were carried down with the precipitate as barium chloride than that they were united with the copper. The results show a fair average of a very large number of determinations of oxygen in various preparations. While with the calcium-copper precipitates I never failed to get an oxidation of the ferrous sulphate or chloride, with the barium-copper precipitates I never got an oxidation greater than in No. 3, II. It is evident that we have here two different compounds, but what the barium precipitate can be I cannot even suggest. I could get no evidence of an excess of oxygen in it in any way. Iodised starch-paper was unchanged when placed near the precipitate moistened with hydrochloric acid; whereas chlorine was freely evolved when the calcium cuprate was thus treated. When treated with sulphuric acid there was no evolution of oxygen, while with the calcium cuprate there was always a lively evolution of gas. When strontium was substituted for barium the same changes of colour took place, excepting a darker, duller, red precipitate was formed. It was necessary to suspend finely-ground crystals of strontium hydroxide in the water on account of its slight solubility.

With barium, strontium, and calcium (when calcium hydroxide solution is used instead of suspended lime) the same changes of colour take place; but in the case of the calcium the red precipitate, which is the final state with the barium and strontium precipitates, is followed by a change to a bulky black precipitate which evolves oxygen for some time, and gradually settles in the solution and changes to a crystalline rose-red precipitate.

The probability of my being unable to continue this investigation, for some time at least, has induced me to publish these very incomplete results in the hope that the beginning I have made will be of use to others who may wish to follow the subject further.

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Amines contained in Suint Waters.—A. Buisine.—The mixture examined by the author contained, in 100 parts of total bases, 95 of ammonia, 4 of monomethylamine, and 1 of trimethylamine.—*Comptes Rendus*, No. 19.

## ON RED AND PURPLE CHLORIDE, BROMIDE AND IODIDE OF SILVER: ON HELIOCHROMY AND ON THE LATENT PHOTOGRAPHIC IMAGE.*

By M. CAREY LEA, Philadelphia.

(Continued rom p. 257.)

### *Photochloride by Action of Alkaline Hypochlorites.*

Black or purple-black chloride is easily obtained by the action of an alkaline hypochlorite on finely divided silver such as obtained by reduction in the wet way. Commercial sodium hypochlorite may be used to act on it. It is to be poured over the silver, and after standing a few minutes is to be replaced with fresh. After an hour or two this is again to be replaced with a new portion, which is to be allowed to act half an hour to insure the total conversion of the silver. The product varies somewhat in colour, is sometimes black, oftener purple-black. If the treatment with hypochlorite has been thorough, strong cold nitric acid of 1·36 sp. gr. extracts from it no silver. This reaction with nitric acid is important, as it shows that not only metallic silver was not present, but that the product contained absolutely no uncombined sub-chloride. For if any were present it would instantly be decomposed by the acid, in which one-half of its silver would dissolve. The action therefore appears to take place in this way. First sub-chloride is formed; part of this is further chlorised into normal chloride which at once combines with other sub-chloride, thus taking it out of the further immediate action of the hypochlorite, and this goes on until an equilibrium is reached and neither metallic silver nor uncombined sub-chloride is left, as is proved by the action of nitric acid. Alkaline hypochlorite, as will presently be shown, attacks uncombined sub-chloride very rapidly, the combined very slowly; by many days' contact the quantity of combined sub-chloride is gradually reduced.

Prolonged treatment with hot strong nitric acid destroys all the varieties of photo-chloride. The time needed varies a good deal. A specimen of that obtained with hypochlorite required twenty-five hours' heating with acid of 1·36 in a water-bath at 212° F. to bring it to the condition of white normal chloride. Considering that cold dilute nitric acid instantly destroys freshly precipitated argentous chloride in the free state, this long resistance to strong acid at the temperature of boiling water must be considered most remarkable.

When the red or photo-chloride is formed with the aid of a ferrous salt or ferrous oxide, I prefer to boil the product with dilute HCl to get rid of the last traces of iron, after a preliminary treatment with hot dilute nitric acid has removed silver and uncombined sub-chloride. The photo-chloride will sometimes even resist boiling aqua regia for a time.

Protected from light, photo-chloride is perfectly stable. Specimens obtained eighteen months ago appear to be quite unchanged.

When treated with ammonia, it is far more slowly attacked than the normal. The ammonia dissolves the normal chloride only. The union between the two must therefore be broken up, and this takes place slowly. The first action of the ammonia is to change the red or purple colour to greenish black and then to slowly dissolve out silver chloride. Hours are required even with a large excess of ammonia. Whilst this is going on, if the ammonia is poured off and replaced with nitric acid, the original colour reappears. If the action is continued sufficiently long, silver only remains and dissolves readily in nitric acid. A little short of this, treatment with nitric acid leaves a black residue of dark chloride mixed with metallic silver; the dark chloride being insoluble in any acid has led to some strange mistakes in a similar reaction

* *Amer. Journ. of Science*, 3rd Series, vol. xxxiii., p. 349.

which occurs in treating with ammonia silver chloride that has been exposed to the light. Even a theory has been had recourse to of a "passive condition" of silver. This passive silver is simply black chloride.

A specimen of purple black chloride was treated with warm strong aqua regia until whitened by conversion of the sub-chloride to normal. By this treatment 2·563 grms. of photo-chloride gained 9 m.grms., indicating the presence of 2½ per cent of sub-chloride, or more exactly—

| | |
|---|---|
| Sub-chloride .. .. .. .. | 2·49 |
| Normal chloride .. .. .. | 97·51 |

This is not to be taken in any sense as representing a constant composition. The proportion of sub-chloride varies between certain limits, not only according to the method of preparation used but independently of it. Another specimen of black chloride formed with hypochlorite gave figures that indicated a content of less than half of one per cent of sub-chloride.

*Photo-chloride by Reduction of Normal Chloride.*

This is an excellent means of obtaining red chloride. The white chloride is to be dissolved in ammonia and ferrous sulphate added, producing an intensely black precipitate. After standing a minute, the mixture is to be treated with dilute sulphuric acid until it shows a strong acid reaction.

The precipitate is to be first well washed by decantation, then boiled first with dilute nitric, then after washing with dilute hydrochloric acid, which must of course be thoroughly washed out.

The product obtained in this way is often of singular beauty. It might easily be taken for metallic copper. Sometimes it is as rich and bright in colour as the copper obtained by electric deposition. Everyone knows the richness and brilliancy of that form of copper, and I have seen it fully equalled by this silver salt.

The beauty of the colour depends always on the thorough removal of any metallic silver that may be present, and still more on getting rid of every trace of iron. The boiling with dilute hydrochloric acid should be continued until, after thorough washing, a fresh treatment extracts no more and the acid remains colourless in presence of alkaline sulphocyanide.

Instead of an ammoniacal solution of silver chloride, we may make a solution of any other silver salt in ammonia and reduce it in the manner just described with ferrous sulphate. But in this case hydrochloric acid must be used instead of sulphuric after the reduction. This single reaction includes an almost endless variety of methods. The acid with which the silver was originally combined seems to be not without influence on the result; in some cases, for example, with arseniate and molybdate, the action of coloured light on the red chloride seems to be somewhat modified. Silver phosphate, on account of the ease with which it suffers reduction, is very well adapted for this treatment.

*Photo-chloride by Partial Reduction of Oxide by Heat, and Treatment with* HCl.

This method has the advantage of avoiding all admixture of foreign substances, the last traces of which are very hard to get rid of, and seem to exert an effect on the colour disproportionate to their quantity. Accordingly the photo-chloride obtained in this way is very beautiful, the shades are from pink to copper red, and a tint resembling burnt carmine.

Heat may be applied to the oxide in either of two ways, long continued heat at 212° F., or near it; or the change may be effected by roasting.

When slow heat is to be applied care must be taken that the oxide does not carbonate itself, which it easily does superficially; this is an objection because the carbonate, under these circumstances, yields white chloride with which the other becomes mixed. The air of a drying oven heated by a gas burner is especially bad in this respect. I have seen a surface of oxide form a coat of yellow carbonate in a few hours in this way. (Most oxide that has been kept some time will effervesce briskly with an acid.) The method is uncertain, sometimes giving strongly coloured products and sometimes pale pink.

The oxide may be roasted in a shallow flat-bottomed porcelain basis. With a very moderate heat it changes from brown to black. When this is thoroughly accomplished and before grey reduction sets in, the oxide is to be treated with HCl. If this be done in the basin itself after cooling and without disturbing the position of the oxide, a curious variety of tints will be noticeable, depending upon slight differences in the heat affecting different portions.

*Silver Carbonate* may be roasted in the same way as silver oxide, and yields a similar product. By heat its colour changes from yellow to black; it is probable that the carbonic acid is driven off at a lower temperature than that at which oxide is reduced to silver, and that with it escapes part of the oxygen. The residue is converted by HCl into deep red chloride.

(To be continued.)

## PROCEEDINGS OF SOCIETIES.

### THE ROYAL SOCIETY.

The following were amongst the principal objects of interest at the Royal Society *Conversazione* on Wednesday June 8th:—

*Apparatus for Shooting Threads of Glass, Emerald, Quartz, &c.*—Exhibited by Mr. C. V. Boys, A.R.S.M.

A thin rod of the material is fastened to the tail of an arrow and heated at the end by an oxyhydrogen flame. The trigger of a cross-bow is immediately pulled, and the arrow shot, when a thread of extreme fineness is drawn out. These threads are far finer than spun glass, and many are finer than spider lines. Threads of quartz are practically free from elastic fatigue, and are most suitable for the torsion threads of instruments of precision. Quartz can be drawn so fine that the thinnest parts are beyond the power of any possible microscope to define them.

*Optical Experiments.*—Exhibited by Prof. A. W. Rücker, F.R.S.:—

1. Colours of Soap Films Rotating under the Influence of an Air Current.

A jet of air is directed on to the film so as to form a vortex, the colours of which change as the film becomes thinner. This experiment is due to Sir David Brewster. Attention has been recently called to it by Lord Rayleigh, Sec. R.S.

2. Artificial Imitation of the Colours of the Setting Sun.

Light is passed through a glass cell containing a solution of sodium hyposulphite. If a little hydrochloric acid is added, the sulphur is deposited in fine particles which scatter the blue end of the spectrum. The transmitted light becomes redder, and colours like those of sunset are produced. This experiment is due to Captain Abney, F.R.S.

3. Apparatus to illustrate the Passage of Light through Lenses.

An application on a large scale of the method of tracing the rays by passing them through air in a close space charged with a small quantity of smoke.

*Some of Dr. J. Puluj's Vacuum Tubes, made by Müller, of Bonn.*—Exhibited by Mr. Warren de la Rue, F.R.S., and Dr. Hugo Müller, F.R.S.

(1) Electrical radiometer with phosphorescent vanes.
(2) Electrical radiometer with phosphorescent rotating disc.

(3) Electrical radiometer with two phosphorescent rotating discs.
(4) Electrical radiometer with rotating bell glass.
(5) Phosphorescent lamp.

*Electric Irradiation of Precious Stones, Minerals, and Rare Earths in Radiant Matter Tubes.*— Exhibited by Mr. WILLIAM CROOKES, F.R.S., Pres. C.S.

A large induction-coil, containing about 60 miles of secondary wire, and capable of giving a 24-inch spark, is used to produce phosphorescence of the contents of the highly exhausted Tubes.

The Great Yellow Diamond from South Africa. Weight 116 carats. Fluorescent.—Lent by Mr. Streeter.

Fluorescent Diamond (Indian).— Phosphoresces yellowish grren.

Cape Diamonds.—Phosphoresce blue.

Brazilian Diamonds.—Phosphoresce red, orange, blue, and yellow.

Australian Diamonds.—Phosphoresce yellow, blue, and green.

Large Ruby from the Burmah Mines; Clusters of Uncut Rubies from Burmah; Cut Rubies Mounted; Artificial Rubies.—Phosphoresce of a brilliant crimson.

Topaz.—Phosphoresces blue.

Sapphire.—Phosphoresces green.

Spinel.—Phosphoresces with a crimson light.

Phenakite.—Usually phosphoresces blue. Occasionally a crystal is found which phosphoresces yellow.

Pectolite.—Phosphoresces of a straw colour.

Calcite.—Phosphoresces of an orange colour.

Phosphorescent Calcite from Branchville, S. Carolina.—When heated in air it has the curious property of glowing strongly with a golden yellow light. In the Radiant Matter Tube this phosphorescence is very brilliant.

Spodumene.—Phosphoresces of a yellow colour. A phosphorescing crystal of Spodumene has all the internal light cut off with a Nicol prism when the long axes of the Nicol and the crystal are parallel.

Dolomite.—A granular form from Utah; when scratched with a knife or struck with a pick it emits so strong a phosphorescent red light that the miners call it Hell-fire Rock. In the Radiant Matter Tube it glows with a fine red light.

Aluminium Oxide, Calcined.—Phosphoresces with a rich crimson light.

Zirconium Oxide, Calcined.— Phosphoresces with a bluish white light.

Strontium Oxide, Calcined.—Phosphoresces with a fine blue light.

Glucinum Oxide, Calcined.—Phosphoresces with a faint blue light.

Calcium Sulphide.—Phosphoresces blue, yellow, green, or red, according to the mode of preparation.

Yttrium Sulphate.—Phosphoresces with a golden yellow light. Examined with a spectroscope gives a remarkable discontinuous spectrum.

Samarium and Calcium Sulphate.—Phosphoresces with a red light, and gives a spectrum composed of three broad bands.

Apparatus illustrating the Supposed "New Force" of M. J. Thore.

*Exhibited by* Prof. J. NORMAN LOCKYER, F.R.S.:—

1. Experiments showing the difference between Line and Fluted Spectra.

A mixture of salts of sodium, lithium, and thallium, raised to incandescence in the flame of a Bunsen's burner, furnishes a convenient example of a line spectrum, the spectrum in this case consisting of a double yellow, a red, and a green line.

Carbon compounds, enclosed in so-called vacuum tubes, and raised to incandescence by a succession of sparks from an induction coil, give us very beautiful sets of flutings shading off towards the violet. The gases enclosed in the tubes are carbon monoxide and benzine. The tubes were filled in the usual way by connecting one end with a Sprengel's air-pump and the other with an apparatus for generating the gas or vapour, all joints, stopcocks, &c., being rendered air-tight by mercury joints. When the gas was pure and at a convenient pressure, the tube was sealed off with a blowpipe. In sealed tubes of this kind, variations of temperature can usually only be obiained by the use of a Leyden jar or jar and air-break; but in laboratory experiments, where the tube is left in connection with the air-pump, temperature can also be varied by changes in pressure. In tubes of the form exhibited, however, considerable variation can also be obtained by changing the length of the spark, and by using the capillary or wide part of the tube, as the case may be. It will be observed that, at different temperatures, different sets of flutings of carbon make their appearance.

2. Photographs showing Line and Fluted Spectra.

The fluted spectrum exhibited is one of the sets of carbon flutings which occurs in the spectrum of the electric ark.

The line spectra are the spectra of various metals, the metals or their salts being raised to incandescence in the electric arc, and their spectra photographed.

*Exhibited by* Prof. JOHN M. THOMSON:—

1. Experiments with Coated Crystals in different Solutions.

These illustrate (*a*) the production of substances not usually obtained artificially in the crystalline condition; (*c*) the formation of crystals through narrow orifices or cracks; (*d*) the probable manner in which certain natural crystalline minerals are formed.

1. Silver dichromate growing from potassium dichromate, coated with paraffin, suspended in silver nitrate.

2. Lead chromate from coated potassium dichromate in lead nitrate.

2. Experiments with Supersaturated Solutions.

(*a*) Tubes containing solutions of heteromorphous salts (sodium acetate and thiosulphate). Either of these solutions may be solidified independently of the other by dropping in a crystal of the particular salt in solution.

(*b*) Flasks containing different supersaturated solutions for experimenting with.

## CHEMICAL SOCIETY.

*Ordinary Meeting, June 2nd, 1887.*

Mr. WILLIAM CROOKES, F.R.S., President, in the Chair.

THE PRESIDENT announced that the Council had resolved to present an Address of Congratulation to the Queen.

Certificates were read for the first time in favour of Messrs. William Elborne, Owens College, Manchester; and Herbert B. Stocks, 13, Peet Street, Liverpool.

The following papers were read:—

51. "*The Equivalent of Zinc.*" By Lieut.-Colonel REYNOLDS, late R.E., and Prof. W. RAMSAY.

The determination has been made by measuring the hydrogen evolved on dissolving zinc in acid, every precaution being taken to ensure accuracy; the weight of the hydrogen obtained was deduced from Regnault's determination of the density of hydrogen. The zinc used was separated by electrolysis from zinc sulphate, purified to the utmost possible extent; the last sample prepared was so nearly pure that dilute acid would scarcely act on it.

In all twenty-nine experiments were made. Four experiments had to be rejected; nine were not fully

corrected, and therefore were also rejected; the next eleven were considered preliminary, the mean atomic weight deduced from them being being 65·2430; finally, five experiments were completed, and the following results obtained from these are free from all known sources of error:—

65·5060
65·4766
65·4450
65·5522
65·4141

Mean .. 65·4787 ± 0·016135

Full details are given in the paper.

52. "*The Magnetic Rotation produced by Chloral, Chloral Hydrate, and Hydrated Aldehyde.*" By W. H. Perkin, Ph.D., F.R.S.

The author has shown in a previous paper (*Chem. Soc. Tr.*, 1886, 777) that when water unites with another substance so as to produce an atomic and not a molecular compound, the magnetic rotatory power of the product is less than the sum of the magnetic rotatory powers of the compounds used in its formation. He has now applied the same method of examination to aldehyde and chloral and their hydrates.

Chloral hydrate was examined (*a*) in the fused state at 55·5°; and at the ordinary temperature (*b*) dissolved in water in the proportion of 1 mol. to 3 mols. of water, and (*c*) dissolved in a new neutral liquid isoamyl oxide. Deducting from the values found that deduced for liquid chloral, the results are as follows:—

| | Fused at 55·5°. | In water. | In amyl oxide |
|---|---|---|---|
| Chloral hydrate .. | 7·173 | 7·016 | 7·028 |
| Chloral .. .. .. | 6·590 | 6·590 | 6·590 |
| | 0·583 | 0·426 | 0·438 |

From these numbers it is evident that chloral hydrate does not contain water as a constituent, as in that case the difference should be 1·00.

As ethylidene glycol, $CH_3{\cdot}CH(OH)_2$, is not known at any rate in a pure state, its magnetic rotatory power was deduced from that of some of its derivatives (*Chem. Soc. Trans.*, 1884, 571). Deducting from the most probable value (2·817) that of aldehyde (2·385), a difference results (0·432) which is practically identical with those found in the case of chloral hydrate at low temperatures. The result obtained with fused chloral hydrate at 55·5° is a little higher, but there is no doubt that the hydrate is slightly dissociated when heated to this temperature: that this is the case is further indicated by a series of determinations of the density of a solution of chloral hydrate in amyl oxide between 4° and 60°, a change in the curve obtained on plotting the results being seen to occur at a point corresponding to a temperature a good deal below 55·5°.

Experiments were also made with mixtures of aldehyde and water, that generally used consisting of equimolecular proportions. On making this mixture of aldehyde and water some interesting peculiarities were noticed. If the temperature of the air and of the liquids be about 8° or 9°, at the moment of mixing the temperature drops about 1·5°; it then commences to rise somewhat quickly, and continues to rise, but more and more slowly, for a long time: in one experiment, made in a large test-tube covered with cotton-wool, commencing at 9° the temperature rose to 18·7° but only in the course of twenty-five minutes. If the temperature of the substances before admixture be about 16°, and the quantities not too small, the rise of temperature is more rapid and the mixture enters into ebullition.

On attempting to determine the density of the mixture of aldehyde and water, the results obtained were at first very perplexing, from the fact that concordant numbers could not be obtained. It was then found that when any change of temperature took place the volume did not become constant in less than two and a half to three hours, so that in determining the density it was necessary to keep the tube containing the mixture at the desired temperature for two and a half hours before adjusting. Part of the product evidently undergoes dissociation as the temperature rises, re-combination taking place as the temperature falls, but only very gradually, a small variation of temperature sufficing to produce a disturbance.

Comparing the magnetic rotatory power of aldehyde with that of the mixture with water at 16°, the difference 0·929 = 3·324 − 2·385 is less than 1·00, and it may therefore be concluded that combination takes place; at a lower temperature no doubt this combination would have been found to be more perfect. There can, however, be no doubt that ethylidene glycol is present in the mixture.

Glycols are viscid fluids, and it is interesting to notice that when the hydrated aldehyde is shaken up, a froth forms which does not break at once, the mixture differing in this respect from aldehyde and also from water.

The effect of mixing aldehyde and absolute alcohol in molecular proportions is also very interesting. If the temperature of the liquids be not too low, the temperature rapidly rises and the mixture boils; if, however, the temperature be low, say 8° or 10°, the temperature immediately falls seven or more degrees; the rise then sets in, and before long the mixture reaches its boiling-point. In the first instance the fall is due to what may be called molecular arrangement setting in between the two fluids, which is a physical change and occurs before chemical action has had time to take place to any appreciable extent; then chemical action takes place more and more rapidly, and in consequence the temperature rises.

On mixing pure dry ether with aldehyde a fall of temperature occurs; subsequently the temperature rises gradually, but only to that of the surrounding air.

53. "*Note on a New Class of Voltaic Combinations in which Oxidisable Metals are replaced by Alterable Solutions.*" By C. R. Alder Wright and C. Thompson.

It appeared to the authors probable that just as a liquid capable of parting with oxygen, chlorine, &c., can be used in conjunction with an electrode of unchangeable material at one side of a voltaic cell (as in Grove's nitric acid battery and analogous combinations), or may be replaced by a solid conducting electrode, itself capable of losing oxygen (*e.g.*, a plate of strongly compressed peroxide of lead), so conversely might a conducting plate of oxidisable material (*e.g.*, zinc) at the other side be replaced by an unchangeable electrode in conjunction with a liquid capable of taking up oxygen, chlorine, &c., without producing any fundamental change in the character of the actions taking place in the cell whilst generating a current. The electrode immersed in this oxidisable substance, like the zinc of an ordinary cell, would acquire the lower potential, and the opposed plate the higher potential; *i.e.*, the wire connected with the latter would be the "positive pole" of the construction in reference to the external circuit.

On trial it has been found that such is the case, and that in consequence a large variety of novel forms of cell becomes easy of construction. For example, sodium sulphite or potassium ferrocyanide solution opposed to chromic-sulphuric acid solution; preferably with an intermediate layer of some neutral salt solution, such as sodium sulphate, to prevent the direct action of the two fluids on one another. During the passage of a current sodium sulphate or potassium ferricyanide is formed in quantity proportionate to the electricity passing, *i.e.*, to the amount of silver thrown down in a silver voltameter included in the circuit, whilst chromium sulphate is produced at the other side. Various analogous cells are described, in particular one where lead oxide dissolved in caustic soda is opposed to alkaline hypobromite: in this case lead dioxide is produced and separates out in the solid form; and one where chromium sesquioxide dissolved in caustic soda is opposed to chromium trioxide dissolved

in sulphuric acid; here sodium chromate and chromium sulphate are formed, an E.M.F. about equal to that of a Daniell cell being set up.

DISCUSSION.

Mr. PAGE said that after listening to Dr. Wright he was able for the first time to understand how electric currents might arise in the animal body.

Dr. ALDER WRIGHT said in reply to Mr. Page that the experiment suggested of opposing venous and arterial blood had not been actually tried by him as yet, but he thought it quite probable that a weak current might be produced (the PRESIDENT subsequently said that he had been told—he believed by Mr. Peter Squire—that a current was produced on opposing venous and arterial blood). By opposing alkaline pyrogallol solution to oxidising agents, notable currents could be developed; and various other organic compounds might be used instead of pyrogallol. With certain organic bodies, however (*e.g.*, chloral hydrate), attempts to produce oxidation in cells had hitherto failed. The opposition of acid and alkaline fluids alone would not necessarily produce more than infinitesimal currents; Becquerel's "*pile à oxygène*" (nitric acid opposed to caustic potash solution) gave rise to decomposition of nitric acid and evolution of oxygen from the electrode immersed in the alkali; other authors had found that analogous cells with chromic-sulphuric acid instead of nitric acid would behave in the same way and develop a continuous current capable of doing external electrolytic work, such as deposition of silver in a voltameter; on the other hand, a cell in which caustic soda and sulphuric acid only were opposed (so that chemical action other than neutralisation could not take place) would only develop an infinitesimal current through a silver voltameter, capable of depositing only traces of silver even after some days, although its E.M.F. measured by an electrometer was considerable.

With regard to the observations of Dr. Armstrong, he would say that while without doubt Grove's gas battery was the prototype of the class of cells discussed, inasmuch as that combination was virtually an oxidisable solution of hydrogen opposed to an oxidising solution of free oxygen, still the examination of cells in which other oxidisable fluids were used instead of hydrogen solution, and other oxidising substances besides solution of oxygen, was a branch of experiment in which hardly anything had hitherto been done, and which seemed to merit some little attention. The authors desired to study in detail the general behaviour of certain typical classes of cells in which actions of the kind take place, especially from the point of view of elucidating the precise chemical changes going on and their relations to the amounts of electrical (or current) energy developed. Whilst there was not exactly a probability of any very startling discovery being made, there were still a number of points of interest connected with the subject worth examining; and although the hope of an improved primary battery based on actions of this kind for commercial use, as suggested by the President, was perhaps not yet within measurable distance, yet the problem of economically obtaining current energy by direct chemical action (and especially by oxidation) was one now attracting considerable attention, and it was impossible to predict what might or might not be the result of systematic experiments tending in that direction. The importance of obtaining practically usable currents from coal direct without the use of the steam engine and dynamo could hardly be over-rated should it hereafter be found practicable so to do; and in view of the compactness of the animal machinery, whereby the oxidation of fuel in the form of food gave rise by muscular action to mechanical energy, it did not seem to be of necessity hopeless to attempt to solve such a problem.

54. "*The Composition of Prussian Blue and Turnbull's Blue.*" By EDGAR F. REYNOLDS.

According to Williamson, these componnds are respectively represented by the formulæ $Fe_7Cy_{18}$ and $Fe_5Cy_{12}$, but Reindel and others have conjectured that they are identical in composition. The author has carefully prepared Prussian blue from hydrogen ferrocyanide and ferric chloride, and Turnbull's blue from hydrogen ferricyanide and ferrous sulphate; his analyses of the products show that Williamson's formulæ are correct expressions of their composition.

55. "*Phlorizin.*" By Professor E. H. RENNIE, D.Sc.

The author has endeavoured by a re-examination of phlorizin to decide as to the correctness or otherwise of the usual formula, and also to ascertain whether the sugar yielded by it on hydrolysis is really dextrose or not. He shows by analyses and by a quantitative examination of the decomposition by dilute sulphuric acid that the usualty accepted formula and equation correctly describe the composition and hydrolysis of phlorizin. The sugar obtained from it melted at 85° to 86°; its molecular rotatory power was $[\alpha]_D = 57{\cdot}9°$; and it gave with phenylhydrazine hydrochloride a yellow crystalline precipitate melting at 204 to 205°: there can be little doubt, therefore, that it is ordinary dextrose.

56. "*Further Notes on the Chemical Action of Bacterium Aceti.*" By ADRIAN J. BROWN.

The author has continued his studies on the oxidising actions of *B. aceti*, and states that although mannitol has been shown to be easily converted into lævulose by the organism, its isomeride, dulcitol, is not acted upon.

The dihydric alcohol, glycol, is oxidised into glycollic acid, no further product being formed. The action is carried on much further when calcic carbonate is present to neutralise the acid as it is formed.

The trihydric alcohol, glycerol, is found to be completely decomposed into carbon dioxide and water, the only other product formed being a very small amount of an acid the identity of which could not be determined. Glycerol appears to encourage the growth of *B. aceti* more than any other substance with which the author has experimented.

The tetrahydric alcohol, erythrol, resists the action of the organism. Attention is called to the fact that erythrol and methylic alcohol are both acted on by oxygen in presence of platinum-black, but escape oxidation when placed under the influence of *B. aceti*; it is also shown that when the same substance is submitted to oxidation in the two ways, the products are generally dissimilar, as in the cases of mannitol and dextrose. It is therefore considered that although the products of the actions which occur in presence of both platinum-black and *B. aceti* are similar in the case of ethylic alcohol, the manner in which the oxidation is effected, contrary to the usual idea, is probably quite different.

Mannitol has been prepared by the author from pure dextrose by the action of sodium amalgam. On submitting this to the action of *B. aceti* it was converted into lævulose, thus completing the conversion of dextrose into lævulose. As the melting point and crystalline form of mannitol from dextrose are similar to those of mannitol from manna, there can be little doubt that the two mannitols are identical.

57. "*Note on the Cellulose formed by Bacterium xylinum.*" By ADRIAN J. BROWN.

The author showed in a previous paper (*Chem. Soc. Trans.*, 1886, 432), that an acetic ferment, *B. xylinum*, is able to convert lævulose into cellulose. On treating this cellulose with strong sulphuric acid, it is found to be converted into a dextrorotary sugar, and in this respect to resemble ordinary cellulose.

58. "*The Oxidation of Ethyl Alcohol in the Presence of Turpentine.*" By C. E. STEEDMAN, Williamstown, Victoria.

The author finds that dilute ethyl alcohol in the presence of air and turpentine becomes oxidised to acetic acid. The experiment was made by placing in a clear glass 16-oz. bottle a mixture of 2 drams of alcohol, 1 dram of turpentine, and 1 oz. of water; the bottle was securely corked and left exposed to a varying temperature averaging about

80° F. for three months; at the end of that time the liquid was strongly acid from the presence of acetic acid.

One curious fact appears to have light thrown upon it by this observation. Mr. McAlpine, Professor of Biology at Ormond College, Melbourne University, has a method of preserving biological specimens by abstracting their moisture with alcohol after hardening in chromic acid, and then placing the specimen in turpentine for some time; great discrepancies arise, however, according as the alcohol is allowed or not to evaporate from the specimen before dipping it into turpentine.

At the next Meeting on June 16th there will be a ballot for the election of Fellows, and a list of the Papers to be read is given at p. 272.

## NOTICES OF BOOKS.

*Nitrate of Soda: its Importance and Use as Manure*, By A. Stutzer, Ph.D. Edited by Prof. P. Wagner. Ph.D. London: Whitaker and Co. 1887.

Nitrogen is one of the most important elements on which plants depend for their sustenance: it is as necessary to their existence as light or rain; it is found in the roots, leaves, seed, and wood, and is also an element in the formation of *protein*, to produce which is the principal object of agriculture. In his essay on this subject, under the above title, Mr. Stutzer has carefully reasoned and discussed the question as to how nitrogen should be best applied. Farmyard manure is in very few cases sufficiently rich to supply the necessary quantity, and recourse must be had to other sources. It has been proved that plants cannot thrive unless nitrogen is supplied to the roots. In the experiments of Lawes and Gilbert crops were obtained from the same plot of land for more than twenty-five years without the addition of any nitrogen in the form of manure, and it has been equally shown that nitrogen is not absorbed by the plant from the air; hence in this case the ammonia and other nitrogenous matter in the air must have been carried down by the rain into the soil, and so reached the roots.

The principal artificial nitrogenous manures are nitrate of soda, sulphate of ammonia, and animal refuse. The first is the most important, and its exportation from South America has been increasing enormously during the last fifty years.

In the chapter on the supposed exhaustion of the soil, following the use of nitrate of soda, it is pointed out that the alleged deterioration is caused simply by the increased crop having absorbed more potash and phosphoric acid than an ordinary or poor crop would have done. The crop itself does not contain a larger percentage of these two substances, but the soil is exhausted simply in proportion to the increase of the crop.

It is of course well known that manure best suitable to one plant cannot be so advantageously employed with another. To show the varying effects of nitrate of soda Mr. Stutzer has given the results of a number of trials in tabular form, and we find that the increase in value of different crops varies from 11 in the case of hay to 35 in the case of potatoes.

This is an important subject, but one which has not yet been properly considered: it, however, resolves itself into finding what is the receptive power of plants for this manure.

The second part of this pamphlet considers the question of how nitrate of soda can best be used as a manure as regards mixture with other manures, quantities required, time of application, and the requirements of different crops, plants, and trees.

The Appendix gives a series of tables containing the results of the trials and experiments above referred to.

To all who are concerned in agriculture, either experimentally or as a business, this book will be of great interest, and we doubt not of real service. The recommendations and hints given are to be relied on as the outcome of careful investigation and a thorough knowledge of the subject.

*England as a Petroleum Power, or the Petroleum Fields of the British Empire.* By Charles Marvin. London: R. Anderson and Co. 1887.

The petroleum industry of the world is one which is yearly assuming more and more importance: its influence has already been felt in a serious manner by those engaged in the palm- and whale-oil trades, and in another ten years it may make a complete revolution in the generation of steam, especially on steamboats, and thus affect the coal industry.

The great Russian oil-wells at Baku afford a striking example of what can be done by capital and engineering skill combined. Ten years ago these wells were quite undeveloped, and even at the end of the Turkish war in 1878—when the Nobles were taking up the question of working them scientifically—the European petroleum world was ignorant of their existence. Now the export has reached 115 million gallons yearly.

The kingdom of Burmah, recently annexed by England, contains petroleum fields equalling, if not exceeding, in richness any others in the world. They have been worked in a dilatory kind of way for centuries: 100 years ago there were 500 wells in operation, producing more than 90,000 tons of oil annually. During the reign of King Theebaw all manners of restrictions were placed on the trade, and excessive royalties were exacted: this, combined with the competition of the American oil fields, has had a most depressing effect, and the annual production has sunk to little over 10,000 tons. English enterprise ought not to allow this state of depression to exist, in view of the enormous importance petroleum will be to the Empire in the near future. We are, however, fortunately situated, for, besides the Burmese oil fields, we have petroleum occurring in India, in districts where there is no coal; we have, again, large deposits of shale in England stretching from the Eastern Counties right up into Scotland, and vast supplies have been discovered in New South Wales, yielding twice as much oil as that found in Scotland; so it may be assumed that our prospects as a petroleum power are excellent; but the matter must not be allowed to rest, other nations are attacking the subject vigorously, and England must show that she can still hold her own in any new industry, wherever it may be situated.

## CORRESPONDENCE.

### DEPOSITS OF PHOSPHATE IN ITALY.

*To the Editor of the Chemical News.*

Sir,—I have been very well pleased in perusing the article on the above subject by Mr. Konrad Walter (Chemical News, vol. lv., p. 229), and I need hardly say that I agree with all that he says concerning the possibility of introducing chemical industries into Italy.

I quite agree with him also that, as far as chemical manufactures are concerned, my compatriots, especially of the South of Italy, have not sufficiently recognised the importance of utilising the rich mineral treasures which are found on the spot. The plain fact is that chemical manufacturing is scarcely as yet understood there, although there are a few bright examples here and there of enterprising spirit shown in that direction.

It has been my aim for years to see that new chemical industries should be started in Italy, and am therefore

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very glad that Mr. Walter comes forward with his practical proposal of establishing the manufacture of superphosphates at Gallipoli, where sulphuric acid would also be produced, and I heartily hope he will induce some enterprising English capitalists to take the matter in hand.

As Gallipoli is situated on the sea-shore the proposed works would be well situated: there is, besides, the advantage for Englishmen of being near their favourite element, the sea. Gallipoli is also well known for its exportation of olive oil, and consequently for the numerous oil factories.

I had opportunity, about four years ago, to visit Taranto (the old *Tarentus* of the Magna Græcia of historical renown), in connection with an oil works for extracting oil from the expressed olive-seed by means of bisulphide of carbon, and was struck by the enterprising commercial spirit of the leading firms there, and was pleased to see works which had been put up and constructed on the best possible modern principles.

Considering the great cordiality existing between the English people and the Italians, I heartily hope that English chemical manufacturers will settle in Italy, where in many cases they will find an almost virgin soil, and be free from the keen competition and hard struggle for existence which is just now the order of the day in the great English chemical industry.—I am, &c.,

A. Sansone.

Vauxhall Chemical Works, Collyhurst, Manchester, May 31, 1887.

## THE SUPPOSED "NEW FORCE."

*To the Editor of the Chemical News.*

Sir,—It might be well to place a cat in front of the apparatus. If the cylinder rotates then it will of course show that the supposed "new force" is not "inherent in the human organism."—I am, &c.,

G. A. Keyworth.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 19, May 9, 1887.

**Researches on the Emission of Ammonia by Vegetable Mould.**—MM. Berthelot and André.—The authors' results apply essentially to the cultivated clay soils of the neighbourhood of Paris. This soil emits spontaneously ammonia by reason of the slow decomposition of the amidic and ammoniacal compounds which it contains. This decomposition is effected at once under the influence of purely chemical actions due to water and earthy carbonates, and doubtless also under the influences of purely physiological actions due to fermentation, to microbia, and to vegetation properly speaking.

**Probable Part played by Magnesia and other Bodies in the Resistance of French and American Vines to the Phylloxera.**—A. C. Dejardin.—Magnesia forms a very important constituent in all soils in which the French vine resists, and in those where the American vine flourishes best. Its percentage in the ash of the American vine is more considerable than in the ash of *V. vinifera*. Practical experiments are needed on the use of magnesium-ammonium phosphate as a manure for vines.

**Reversible Decomposition of the Acetates by Water.**—G. Foussereau.—In former communications the author has studied, by means of the measurement of electric resistances, the reversible decompositions which many metallic chlorides slowly undergo in their solutions under a variety of influences. He has since observed analogous phenomena in iron and aluminium sulphates, in common alum, and in copper, zinc, and lead acetates. These last bodies present some remarkable peculiarities. If their solutions are kept for some time at 100°, or even at lower temperatures, they deposit a basic salt.

**On Glyceric Aldehyd.**—E. Grimaux.—According to Gorup-Besanez, mannite yields a glucose and mannitic acid under the influence of platinum black. The author has applied this process of oxidation to glycerin in order to obtain glyceric aldehyd. As this aldehyd possesses the same composition as glucose, and is at once a polyatomic alcohol and an aldehyd, it remained to be seen if it could be converted into a glucose capable of fermentaction, or if it could be fermented directly. The oxidation products of glycerin by platinum black were found capable of fermentation under the influence of beer-yeast. Carbonic acid is given off and alcohol is formed.

**Synthetic Acetic Acid and its Derivatives.**—Louis Henry.—The author has compared this synthetic acid with ordinary acetic acid, and finds them identical in all respects, both in their reactions and in their derivatives.

**Action of Cyanamide on the Sulpho-conjugated Amidised Aromatic Acids.**—J. Ville.—Sulphanilic acid forms, with cyanamide, an addition product, sulphanilocyamine, analogous to the creatines. This body does not give a dehydration-product corresponding to the creatinines, at least in the ordinary conditions of the formation of these bodies. The study of the isomers will show if this is a property common to the sulpho-conjugated amido acids, due to the acid function $SO_3H$, which does not lend itself to dehydration.

**On Anemonine.**—M. Hanriot.—The author assigns to this substance, which he obtains from *Anemone pulsatilla*, the formula $C_{15}H_{12}O_6$. Besides the portion soluble in alcohol, there remains an insoluble substance having apparently the same composition. Anemonine melts at 156°, and is decomposed at 270°. The author has obtained from it a hydrocarbon (a cumene or a cymene) and also a bromo-anemonine and a hydro-anemonine, the latter much more stable than anemonine itself.

**Certain Derivatives of the Residues of Compressed Gas.**—Albert Colson.—The author finds that the two hexabromides which he has prepared by setting out from erythrite can also be formed by the action of bromine upon synthetic erythrene tetrabromide.

**On Butyl Sebate.**— G. Gehring.— Butyl sebate is a colourless liquid of an agreeable and aromatic odour and a burning taste. It is insoluble in water, miscible in all proportions with alcohol, but less readily with ether. Its density at 0° is 0·9417. It boils, under ordinary pressure, at 344° to 345° without decomposition. A few drops placed on a glass rod burn with a very luminous flame, the nucleus of which is a splended deep blue. Strong sulphuric acid decomposes it, even in the cold. Caustic potassa saponifies it, and ammonia gives a white precipitate of sebamide in microscopic crystals.

**Creatines and the Creatinines; Formation of α-amido-capro-cyamine and α-amido-capro-cyamidine.** — E. Duvillier.— This paper does not admit of useful abridgment.

**Determination of the Carotine contained in the Leaves of Plants.**—A. Arnaud.—The quantity of carotine contained in leaves cannot be neglected. It borders upon 1-10000th of the weight of the dried leaves, and the colour which it imparts modifies completely the tint due to chlorophyll.

**Combination of Hæmatine with Nitric Oxide.**—G. Linossier.—A solution of hæmatine reduced, or of oxyhæmatine in ammoniacal alcohol, absorbs nitrogen dioxide energetically, and becomes of a bright red, not dichroic. If examined with the spectroscope it presents, in place of

the well-known spectrum of hæmatine in an alkaline solution, a spectrum analogous to that of oxyazotised hæmoglobine.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

**Apparatus for Converting Nitrogen Tetroxide into Nitric Acid.**—I wish to know a good form of apparatus for converting nitrogen tetroxide, obtained by heating a heavy metal nitrate, or by the action of water on nitro-sulphuric acid, into nitric acid. The nitrogen tetroxide would, of course, be passed into water, and the resulting nitric oxide be re-oxidised to the tetroxide by mixing with air, and again the tetroxide decomposed by water, and so on, till practically all the tetroxide was converted into nitric acid. M. Schlœsing, in his method for preparing chlorine, decomposes manganese nitrate by heat, and converts the $NO_2$ obtained into nitric acid, re-obtaining about 90 per cent of the original nitric acid. Would you kindly say if there is a recognised form of apparatus for such a process on the large scale?—J. T.

## MEETINGS FOR THE WEEK.

TUESDAY, 14th.—Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
WEDNESDAY, 15th.—Meteorological, 7.
THURSDAY, 16th.—Chemical Society, 8. Ballot for the election of Fellows. "The Thermal Constants of a Liquid Mixture," by Prof. W. Ramsay and S. Young. "Derivatives of Hydrindonaphthene and Tetrahydronaphthalene," by Dr. W. H. Perkin, Jun. "The Formation of Closed Carbon Chains in the Aromatic Series," by F. S. Kipping, B.Sc., and W. H. Perkin, Jun. "The Action of Ethylene Bromide on Ethylic Acetoacetate," by P. C. Freer, Ph.D., and W. H. Perkin, Jun. "Derivatives of Pentamethylene," by H. E. Colman, Ph.D., and W. H. Perkin, Jun. "Derivatives of Hexamethylene," by F. C. Freer, Ph.D., and W. H. Perkin, Jun. "An Attempt to Synthesise a Carbon Ring containing Seven Carbon Atoms," by P. C. Freer, Ph.D., and W. H. Perkin, Jun.
—— Royal, 4.30.

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TO MANUFACTURING CHEMISTS AND OTHERS.

THE METROPOLITAN BOARD OF WORKS will meet at the Office of the Board, Spring Gardens, S.W., on FRIDAY, the 17th day of June, 1887, at Twelve o'clock at noon precisely, and will then be prepared to OPEN TENDERS by parties who may be willing to contract for the supply of 1000 tons of Manganate of Soda and 1000 tons of Chloride of Lime (Bleaching Powder). Parties desirous to submit Tenders, for the whole or part of the foregoing quantities, may obtain a copy of the Specifications, form of Tender, and information as to the places and periods of delivery, on application to the Chemist of the Board, at the Office, Spring Gardens, between the hours of Nine a.m. and Four p.m. (on Saturdays between the hours of Nine a.m. and Two p.m.) until Thursday, the 16th day of June, 1887. The Tenders, which must be on the form supplied from this Office, and addressed to the Clerk of the Board, are to be delivered at the Office before Four o'clock on the last-mentioned day, and no Tender will be received after that hour. The Parties tendering must be in attendance at the Board at Twelve o'clock on the day appointed for opening Tenders, and any Tender which is not fully filled up in every particular will be rejected. The Board do not bind themselves to accept the lowest or any Tender.

Spring Gardens, S.W., 7th June, 1887. J. E. WAKEFIELD, Clerk of the Board.

TOTTENHAM LOCAL BOARD OF HEALTH.

PROTO-SULPHATE OF IRON or GREEN COPPERAS.

The Local Board invite Tenders for the Supply and Delivery at their Sewage Works, Page Green, Tottenham, of PROTO-SULPHATE OF IRON, to be delivered in Five Ton lots as and when required.—Tenders, stating full particulars, to be delivered to the undersigned on or before Wednesday, the 22nd instant. The Board will not be bound to accept the lowest or any Tender.

Dated this 10th day of June, 1887.
By order, EDWARD CROWNE,
Local Board Office, Tottenham, N. Clerk to the Board.

The MIDLAND RAILWAY COMPANY are prepared to receive offers for the purchase of the surplus Ammoniacal Liquor and Tar produced at their Gas Works at Derby and London (Brent) during twelve months ending June 30th, 1888.

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JAMES WILLIAMS,
Derby, June 6, 1887. Secretary.

TIN OXIDE (Moist).—Wanted Address of Makers of this material.—Apply to "Tin Oxide," CHEMICAL NEWS Office, Boy Court, Ludgate Hill, London, E.C.

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THE CHEMICAL NEWS.

Vol. LV. No. 1438.

## HER MAJESTY'S JUBILEE.—A SCIENTIFIC RETROSPECT.

The Jubilee rejoicings upon which we are entering naturally lead us to indulge in a retrospective view of the progress of chemical science during the last half-century, and to survey its present position and its prospects. That position, we must admit, has its lights and its shades.

On the one hand all the facilities and appliances for scientific study are much more accessible and available than ever before. Of text-books, works of reference, and scientific journals there is a perfect plethora. Instruments of precision have been greatly improved, and, as far as practicable, reduced in price. Chemical teaching is winning its way even into schools of the most *arriére* character, and efficient laboratories are being equipped at our universities and technical colleges.

But on the other hand the examinational system is eating its way deeper and deeper into all our educational establishments, and is, by a process of *unnatural* selection, bringing to the front not the most original and creative minds, but those which most rapidly absorb the work of others. A still greater drawback is the political excitement which has prevailed increasingly for the last ten or eleven years, and which more and more draws off public attention from Science.

Nor can it be forgotten that many influential literary men, historians, novelists, poets, and ethicists look upon such studies as physics, chemistry, and biology with ill will. Hence we have little reason to fancy that discovery and invention have entered upon a golden age.

If we compare the respective positions of chemistry in 1837 and in the present year, we see at once strange resemblances and differences still more strange. Very much good work had, indeed, been done. The conception of matter as incapable alike of production or destruction by human agency, or under human experience, had been firmly grasped. The appeal to the balance was everywhere recognised. The notion of the elements as bodies incapable of decomposition or transmutation was held with little question. By far the greater number of these simple bodies—all, indeed, sufficiently abundant to be of practical importance — had been discovered and their atomic weights had been determined with a greater or less degree of accuracy.

As regards the combination of these elements dualism reigned supreme. Indeed, a thinker, who, though no chemist, is still recognised by a certain philosophic sect as the law-giver of all Science, declared, as lately as 1838, that it requires to be universally received in chemistry, and that even organic compounds may be reduced to a succession of binary combinations! The energy with which bodies tended to unite was supposed to depend on their respective distances from each other in the electro-chemical series.

In organic chemistry—as the chemistry of the carbon compounds was then called — the organic bases were being rationally studied. Not only had a number of the vegetable alkaloids been detected and characterised, but the first steps had been taken in the study of the so-called artificial bases, since so fruitful. Aniline had been discovered as far back as 1826 among the products of the destructive distillation of indigo, whilst chinoline was brought to light in 1834. The important hydrocarbon benzol had been recognised by Faraday. Above all, Wœhler, by his artificial preparation of urea, may be said to have effected the first true organic synthesis, and established the continuity of the organic with the inorganic.

We cannot say that in or about the year 1837 there took place any one epoch-making discovery, but the progress of research has become from decade to decade more rapid. The seeds sown in the earlier part of the century have sprung up and borne fruits sometimes not imagined by the sowers.

Turning now from the past to the present, one of the most important changes—not affecting chemistry alone—is that the several disciplines, though by no means losing their respective identities, are being brought into closer mutual relations. This is especially the case as regards chemistry and physics. There is a large and important territory common to both. We find ourselves unable to discuss fundamental questions concerning matter and energy, atoms and molecules, without making use of conceptions belonging to the one as to the other. The great modern doctrine of the conservation of energy—one of the grandest triumphs of the half-century —affects both in an almost equal degree. The law of Avogadro, once little regarded by chemists, now occupies a leading position in theoretical chemistry. No longer can it be said that "physics treats of masses acting at sensible distances, while chemistry treats of molecules acting at insensible distances." The two sciences, acting in concert, have developed a novel means of research, spectral analysis. The value of this method to the astronomer is of the greatest significance as overturning the Comtean dogma that the simpler sciences of his classification are independent of those more complex.

On the opposite frontier biology has undergone novel developments which cannot fail, sooner or later, to throw a new and welcome light upon chemical phenomena. The law of evolution, which has dimly loomed upon us through antiquity and the middle ages, has at last won general recognition, thanks to Darwin and Spencer, and must make itself felt in our science also. Again, the action of minute living beings is now recognised as effecting chemical compositions and decompositions, so that the chemist can no longer ignore biological considerations—a further blow at the Comtean dogma above referred to.

But narrowing our gaze, we must now glance at the growth of general and philosophical chemistry during the half-century just closing. One of the most familiar changes has been the fading away of the Berzelian electro-chemical theory of combination, with its necessary adjunct, dualism, and the recognition of direct multiple combination and of substitution. A little later has followed the attempt to assign to different atoms or groups of atoms forming a compound body, definite positions, and to express and record these positions by means of structural formulæ. All this, together with the changes in nomenclature and notation involved, is still, for the present, known as the "new chemistry."

Great attention has been drawn to the numerous organic syntheses which have been effected. But, however important these results must appear in an industrial and technical point of view, they no longer present the same philosophical interest as does the first step in this direction taken by Wœhler. It is manifest that these discoveries could hardly have been made without a careful study of the relative position of the atoms in compounds.

The detection of the process of dialysis, by Graham, has thrown a much needed light upon a variety of phenomena both in nature and art. Another important step has been the liquefaction and solidification of those so-called permanent gases which had resisted the earlier attempts of Faraday. This discovery is of prime value, not only as upholding the law of continuity, but as elucidating the behaviour of gaseous bodies under pressure and revealing the interesting phenomena of the "critical points."

The study of the behaviour of bodies with reference to light has been rewarded by two discoveries, photography

and spectroscopy, which, if they have not had a great effect upon chemical theory, have supplied every department of science with precious aids in research.

Thermo-chemistry, the study of the heat evolved or absorbed during chemical changes, has been diligently and fruitfully studied, and has coordinated a number of chemical phenomena, which have hitherto seemed desultory and unconnected.

Undoubtedly one of the grandest steps taken in pure chemistry within our epoch has been the discovery of the periodic law. This generalisation, as a reference to our columns will show (Chemical News, vols. vii., x., xii., and xiii.), was in the first place due to our countryman Mr. J. A. R. Newlands. It was some time afterwards independently discovered by Prof. Mendeleeff, and has since been developed both by that eminent savant and by Professors Meyer and Carnelley.

What will be the next great step in scientific chemistry it would be rash to predict. May we venture to hope it will be at least some approach to a demonstration of the compound nature of our conventional "elements," in which direction both experiment and theory seem already pointing?

In our next issue we shall endeavour to summarise the leading features in the progress of analytical chemistry and of the chemical arts.

## NOTE ON THE SOFTENING OF MAGNESIAN WATERS BY CLARK'S PROCESS.

By J. ALFRED WANKLYN.

Committee-Rooms in the Houses of Parliament are sometimes pervaded with an atmosphere which is unfavourable to sound chemistry. On a recent occasion Dr. Frankland, senior, and those who were associated with him in opposition to a Water Bill (which was defeated), pledged themselves to the maintenance of the following assertions:—That it (the Clark process) is not applicable to waters containing a large quantity of magnesia; and that in the particular case of the Sudbrook water—a highly magnesian water—the Clark process would not remove more than one-quarter of the magnesia.

I will place on record direct experiments which I have made, and which negative that which Dr. Frankland laid before the Committee. Sudbrook water contains—

| | Grains per gallon. |
|---|---|
| Carbonate of lime .. .. .. | 13·6 |
| Carbonate of magnesia .. .. | 5·4 |
| Sulphate of magnesia .. .. .. | 3·2 |
| Nitrate of magnesia .. .. .. | 0·6 |
| Chloride of magnesium .. .. | 0·8 |
| Chloride of sodium .. .. .. | 3·5 |
| | 27·1 |

It is highly charged with loosely combined carbonic acid. On submitting the water to the Clark softening process I found that the precipitation by the lime was most satisfactory, the precipitate being easy to remove either by filtration or subsidence.

In my first experiment the total solids in the softened water fell to 11 grains, and contained—

| | | |
|---|---|---|
| CaO .. .. | 3·4 | grains per gallon. |
| MgO .. .. | 1·22 | ,, ,, |

In the second experiment the total solids in the softened water fell to 9½ grains per gallon:—

| | | |
|---|---|---|
| CaO .. .. | 1·57 | grains per gallon. |
| MgO .. .. | 1·44 | ,, ,, |

I have also consulted Mr. Porter, the eminent engineer, who is so successfully working the Clark process on the large scale. He has no difficulty with magnesian waters.

## ON THE DESTRUCTION OF PARASITIC FUNGI BY USING IRON SULPHATE.

By Dr. A. B. GRIFFITHS, F.R.S. (Edin.), F.C.S. (Lond. & Paris Principal and Lecturer on Chemistry, School of Science, Lincoln.

Having been the exponent for the use of iron sulphate (in small quantities) as a manure (see *Journ. Chem. Soc. Trans.*, 1883, '84, '85, '86, '87), the author of this note wishes to allude to several scientific investigators who are using iron sulphate for destroying various micro-organisms which attack farm and other crops.

It will be remembered that the author has shown in several papers the power of iron sulphate as an antiseptic agent for the destruction of *Peronospora infestans* and the "wheat-mildew" (Chemical News, vol. xlix., p. 279); *Journ. Chem. Soc. Trans.*, 1886, p. 119; Chemical News, vol. liii., p. 255; *Chemiker Zeitung*, No. 47).

Several foreign scientific men have also proved the efficacy of ferrous sulphate for the destruction of the large number of fungoid growths which attack the vine. Amongst these are the following:—

1. Recently Dr. F. von Thümen* uses a 10 per cent solution of ferrous sulphate f r the destruction of *Phoma vitis* and *Phoma Cookei*, two fungoid growths which attack the vines of Austria and Hungary.
2. M. Millardet employs 1 kilogrm. of iron sulphate in 2 litres of water, for washing the stocks of vines a fortnight before the shoots begin to start.
   Mme. Ponsort, in Bordelais, uses a mixture of 4 parts of iron sulphate and 20 parts of lime for the same purpose (see Trouessart's "Microbes, Ferments, and Moulds," *Intern. Scientif. Series*, vol. lvii., p. 38).
3. Dr. H. Müller and others (*Biedermann's Centralblatt fur Agricultur-chemie*, 1883, p. 630) have found a solution of 1 part of iron sulphate in 2 parts of water an excellent remedy for destroying *Peronospora viticola*, which attacks the Prussian vines.
4. M. A. Guillamont (*Biedermann's Centralblatt fur Agricultur-chemie*, 1883, p. 272) states that a mixture of 10 parts of iron sulphate, 10 parts of wood-ashes, and 2 parts of coal-tar is a good specific for destroying the Phylloxera.
5. The well-known botanist, Prof. J. von Sachs, of Würzburg University (*Biedermann's Centralblatt fur Agricultur-chemie*, 1886, p. 602), uses iron sulphate for trees and plants generally as a remedy for the disease known as "chlorosis in plants."

In the author's papers already referred to it has been shown that the iron sulphate acts upon the cellulose walls of these parasitic fungi.

These notes may prove useful, for it is not unlikely (owing to the present state of the weather in certain parts of the country) that our farm crops may be attacked by parasitic diseases.

## THE CEMENT INDUSTRY IN ITALY.

By KONRAD WALTER, Chemical Engineer.

There is scarcely anywhere in Europe another country to be found which is, like Italy, by nature rich in building materials of all descriptions. All along the Apennines, especially in Tuscany, and in the Alps, near the Lombardian lakes, we find precious marble in all its varieties; in the Lombardian and Venetian plains there is, in large quantities, excellent clay for the manufacture of bricks and tiles; and in the pre-Alps and Apennines we have

* "Die Phoma-Krankheit der Weinreben verursacht durch die parasitischen Pibze *Phoma vitis* und *Phoma cookei*," von F. v Thümen reviewed in the Chemical News, vol. lv., p. 246).

almost everywhere not only the purest carbonate of lime, but also—and especially in the parts of Bergamo, Lecco, and Arona, and on the hills of Piedmont, in the districts of Casale Monferrato, Alessandria, Vercelli, &c.—an excellent raw material for the manufacture of natural and artificial Portland and Roman cement.

Although these natural treasures exist in almost immeasurable quantities, their industrial application—except the marble industry—is still in a state of infancy. The manufacture of bricks and tiles, with the exception of three or four large establishments, is carried on by hand; the burning of lime is effected almost everywhere in the most primitive kilns, and the manufacture of the valuable Portland and Roman cements is conducted without chemical knowledge in the matter itself, and without regard to economy in fuel and milling expenses.

No wonder, therefore, that Italy has a continual and yearly increasing importation of cements from foreign countries, especially from France, whereas its geographical position, and its almost inexhaustible deposits of the best natural raw material, could make it become an exporting country. In the statistics we find that the importation of cement has been—

| | | |
|---|---|---|
| In 1884 | .. .. | 32,543 tons |
| In 1885 | .. .. | 34,430 ,, |
| In 1886 | .. .. | 39,260 ,, |

whereas in 1879 it was only about 17,000 tons. This is not only proof that the consumption of cements in Italy is increasing from year to year, but also that the home production does not keep up with the increasing demand.

To a certain extent this is due to the little enterprising spirit of the Italians and to the want of capital for industrial enterprises: by far the greatest part, however, is due to the old-fashioned and uneconomical way in which the cement manufacture in Italy is conducted, and the distrust and aversion met with when trying to introduce new inventions and economical processes. In England, Germany, and France, where coal can be had at the works at from 7 to 8 francs per ton, every manufacturer is only too glad to introduce at his works any new improvement by which the smallest saving in fuel can be effected. But if in Italy—where the average price of coal at the works is at present about 30 francs per ton—such improvements are proposed to the manufacturer, the almost general answer is that coal is at present so very cheap, and trade is so bad, that it is not the right time to make experiments and improvements which require an outlay of capital; thereby not considering that this comparatively small outlay of capital is just the thing to improve trade and effect great savings, and that the proposed improvements are not at all problematical experiments, but are introduced already largely and approved of in the most eminent industrial countries.

The Portland cement industry in Italy is even now a good business, but it could be made a first-class one if it were in the hands of intelligent capitalists who would be open to such improvements as could be introduced.

These improvements would be, first of all, the doing away with the old system of furnaces, which have a consumption of above 26 per cent of fuel, and introducing such new systems as, for instance, the furnace Dietzsch, now almost generally used in Europe, and by which scarcely 10 per cent of fuel is used. A further improvement and great saving would be a general re-organisation of the milling of the burnt cement, which up to now has been very costly, by introducing such new mills and crushing machinery as are now used in England,—for instance, the mills of Messrs Morris Brothers, of Doncaster, which effect a saving of more than 50 per cent on the milling cost.

With similar improvements the Portland cement industry in Italy could not only be brought to such a point as to supply all the wants of the country itself, but it could even be extended to exportation, considering the excellent quality and cheapness of the natural raw cement material, which, in spite of the high price of fuel in Italy, would be able to compete with almost any country in Europe as regards quality and cost of production. But even leaving aside the idea of exportation, there ought to be a great future for the Portland cement industry in Italy. All the large projects of river regulation, seaport and harbour, buildings of the Government (which are only in part commenced, and partly to be commenced soon), as well as the really great building projects of Milan, Rome, and Naples, require for the next twenty-five to thirty years such quantities of cement that, even by limiting the production only to the home consumption, enormous profit could be made.

In order to show still more clearly what an excellent business the Portland cement industry in Italy could be, we will only give a few notes regarding the cost of production and actual selling prices.

At Casale Monferrato, where the best Italian Portland cement is made, there are now in use the intermittent kilns and circular furnaces (Hofmann's system), and only one furnace on Dietzch's system is now at work. The consumption of fuel in these three different systems of furnaces is at present per ton of 1000 kilos. of burnt cement:—

In kilns = 279 kilos. of English coke.
In circular furnaces = 237 kilos. of Newcastle coal.
In Dietzsch's furnace = 100 kilos. of small coal.

English coke costs, at the works at Casale, 42 frs. per ton; Newcastle coal, 27 frs.; and small coal, 26 frs.

The expenses of fuel are therefore at Casale Monferrato, per ton of 1000 kilos. of burnt cement,—

| | | |
|---|---|---|
| In the kilns | .. .. .. .. | 11·52 frs. |
| In the circular furnaces | .. | 6·40 ,, |
| In the Dietzsch furnace | .. | 2·60 ,, |

We have therefore in this special case a saving in fuel, in favour of the new system of Dietzsch, of 8·92 frs. against the kilns, and of 3·80 frs. against the circular furnace per ton; and as a double Dietzsch furnace gives an annual production of about 6000 tons of burnt cement, the total saving in fuel alone by the above-named production, and by the use of this system, is 53,520 frs. against kilns, and 22,800 frs. against circular furnaces.

The working cost (expenses for labour) per ton of burnt cement is about the same by all three systems.

Accurately made trials have shown that the Portland cement obtained in the furnaces system of Dietzsch is, as regards quality and mercantile value, not only equal to, but even better than by the other systems.

The saving in milling expenses which can be made by introducing the new mills of Messrs. Morris Brothers, of Doncaster, is also very considerable.

The milling is at present made in stone-mills, and to reduce 20 tons of burnt cement to the fine powder wanted in commerce requires an 80 H.P. steam-engine and a large number of workmen, besides many different auxiliary machines. The expense of reducing a ton of cement to powder is therefore here about 10 frs.

A Morris mill reduces, per working hour, about 1000 kilos. of cement to the finest powder, and requires, together with a Marsden stone-breaker, which breaks up the big pieces to a suitable size for the mill, from 12 to 14 H.P. and very few men. We have therefore more than 50 per cent saving in milling expenses by using this mill.

Milan, May 21, 1887.

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Reproduction of Alabandine.—H. Baubigny.—A solution of manganese acetate, even if slightly acidified with acetic acid, gives an abundant precipitate if treated in the cold with sulphuretted hydrogen. There is formed the well-known rose-coloured sulphide, which, if heated to 100° in a closed vessel, is transformed into the compact green variety. On prolonged standing, crystals are produced, even at common temperatures, and prove to be alabandine.—*Comptes Rendus*, Vol. civ., No. 20.

# ON RED AND PURPLE CHLORIDE, BROMIDE AND IODIDE OF SILVER: ON HELIOCHROMY AND ON THE LATENT PHOTOGRAPHIC IMAGE.*

By M. CAREY LEA, Philadelphia.

(Concluded from p. 267.)

*Action of Various Metallic Oxides on Silver Oxide.*

If we precipitate ferrous oxide with potash and add to this silver oxide, or what amounts to the same thing, if we add to ferrous sulphate potash in excess and pour over this silver nitrate solution, the silver oxide separated by the potash is partly reduced by the ferrous oxide, and when treated with HCl forms red chloride, the intensity of the colour of which depends within certain limits on the amount of reduction of the silver oxide.

Similarly if we treat solution of manganous sulphate with excess of potash and then add silver solution, we get an analogous reaction, except that it is much weaker and heat is necessary.

With chromous oxide the action is still weaker, but evident. With cobaltous oxide it is scarcely perceptible heat and long continued action.

*Action of Ferric Chloride on Metallic Silver.*

It has been long known that silver was blackened by ferric chloride, and this action has been proposed in the text-books as a means of obtaining subchloride, for which it is quite unsuited.

Ferric chloride acts on silver much as sodium hypochlorite does, but less rapidly. With hypochlorite the action is complete in a few hours or often in an hour or less; with ferric chloride one or two days are required before the product ceases to yield silver to hot dilute nitric acid. In both cases the action appears to be alike in this: that no sub-chloride is finally left uncombined with normal chloride.

The product is an intensely dark purple-black, when the action takes place in the cold. With heat continued for many hours, ferric chloride can be made to attack the purple salt and gradually convert it into AgCl. With a strong solution in large excess kept at or near 212° F. for sixty hours the colour was gradually reduced to pink and finally to a dingy pinkish grey. Pure white cannot be obtained, as it can by aqua regia.

In order to observe more exactly the course of the action, a strong solution of ferric chloride was allowed to act on reduced silver in fine powder for four minutes, and then a fresh portion (always in large excess) for the same time. Analysis showed that at this stage of the action the material contained—

| | |
|---|---|
| Ag (determined) .. .. .. | 76·07 |
| Cl (by difference) .. .. .. | 23·93 |
| | 100·00 |

If we suppose that all the silver was combined with chloride, the constitution of the substance would be—

| | |
|---|---|
| AgCl .. .. .. .. .. | 92·49 |
| $Ag_2Cl$ .. .. .. .. .. | 7·51 |
| | 100·00 |

but this was probably not the case; there was almost certainly free silver present, and consequently a less proportion of sub-chloride. Another specimen, treated repeatedly with hot acid until every trace of free silver was removed, was found to contain 1·52 per cent of sub-chloride, colour purple. Another similarly treated contained 7·3 per cent sub-chloride.

*Action of Nitric Acid on Silver Sub-chloride.*

When freshly precipitated and still moist sub-chloride of silver is treated with nitric acid, a sharp effervescence, accompanied with a disengagement of red fumes, sets in; presently the strong red colouration of the photo-chloride appears and the action ceases. This production of the red and not the white chloride in the decomposition of $Ag_2Cl$ is precisely what might have been expected, for when AgCl is formed in the presence of $Ag_2Cl$ more or less combination always takes place.

The action is interesting in this respect: the AgCl first formed is at the moment of formation in presence of all the yet undecomposed portion of $Ag_2Cl$, and whatever part it combines with is removed from the action of the acid. It would therefore seem probable that this method would be one of those that yielded a product having the largest proportion of $Ag_2Cl$, but analysis showed that different specimens were extremely variable—of those analysed, one contained 8·62 per cent of $Ag_2Cl$, another 6·56, and a third 1·96. All that analysis can do with such substances is to fix the limits within which they vary. The quantity of sub-chloride left after treatment with nitric acid depends partly on the strength of the acid and the time for which it is allowed to act, but also to come extent on variations in the resistance of the substance itself. These specimens were of shades between rose and purple.

The colour of any particular specimen is always lightened in shade by abstracting $Ag_2Cl$ from it by continued boiling with nitric acid. But as between different specimens, especially when formed by different reactions, it by no means follows that the darkest in colour contains the most sub-chloride.

Argentous chloride when treated with sodium hypochlorite yields a purple form of photo-chloride. A specimen so treated contained 2·57 per cent of $Ag_2Cl$.

*Action of Cupric Chloride on Silver.*

When metallic silver is submitted to the action of either cupric chloride, or what gives the same result, a mixture of copper sulphate and ammonium chloride, an action takes place very similar to that of ferric chloride, but more energetic, and the resulting red chloride is apt to be lighter in shade, though in this respect it varies very much. As in the case of ferric chloride this action of cupric chloride on silver is given in some text-books as a means of obtaining argentous chloride, for which purpose it is as little suited as the iron salt.

As a mode of obtaining red chloride it is not to be recommended. It is troublesome to get the copper completely removed.

A specimen analysed was found to consist of white chloride with 6·28 per cent of sub-chloride.

*Action of Proto-chlorides on Silver Solutions.*

*Cuprous Chloride.*—When very dilute solution of silver nitrate is poured over cuprous chloride, a bulky black powder results, which by boiling with dilute nitric acid turns red, the acid extracting little or no silver.

*Ferrous Chloride.*—When silver nitrate is dissolved in a slight excess of ammonia, and this solution is poured into a strong one of ferrous chloride there results a precipitate which is sometimes greyish, sometimes olive-black. By washing with dilute sulphuric acid, this product becomes brownish purple, and brightens by boiling with dilute nitric acid. It was found to contain 4·26 per cent of sub-chloride.

*Photo-chloride by Action of Hydrogen.*

When hydrogen is passed over argentic citrate at 212° F., as in Wöhler's process, there results a black or dark brown powder consisting of argentous citrate, metallic silver, and perhaps other substances. When this is treated with hydrochloric acid and subsequently with nitric, the resulting product is photo-chloride, the characteristic colour of which sometimes appears as soon as the HCl is added. But more frequently the material after the action of HCl has precisely the appearance of silver reduced in the wet way, and the red colour appears only after treatment with nitric acid. Even cold dilute acid (by some hours' contact) will isolate the red chloride; boiling acid does so at once.

* *Amer. Journ. of Science*, 3rd Series, vol. xxxiii., p. 349.

Colour, beautiful purple. A specimen analysed was found to consist of normal chloride combined with 3·11 per cent of sub-chloride.

*Photo-chloride by Action of Potash with Oxidisable Organic Substances.*

There is no better method of obtaining photo-chloride than by acting on a salt of silver with potash and certain organic substances. Milk sugar, dextrine, and aldehyd, give particularly good results. Milk sugar acts rapidly, dextrine slowly. Other substances with which, combined with potash, I have obtained chloride, are: gum, tannin, gallotannic acid, manna, glycerin, alcohol, carbolic acid, &c. The number might doubtless be indefinitely multiplied. After the action has reached a proper stage, which with milk sugar is apt to be in less than a minute and with dextrine may take half an hour, HCl is added, whereupon the precipitate changes in appearance but does not exhibit its characteristic colour until after boiling with nitric acid; the best result is obtained when the precipitate, after addition of HCl, has a rich chestnut-brown shade,* which by nitric acid changes to shades of purple and burnt carmine, when milk sugar, dextrine, or aldehyd has been the reducing agent. When the salt of silver employed has been the chloride, of course treatment with HCl is superfluous.

A specimen obtained by acting on silver nitrate with potash and dextrine was found to contain 2·26 per cent of sub-chloride. Another obtained with silver nitrate, potash, and milk sugar contained only 0·34 per cent. As in former instances these determinations are useful only in indicating the extreme variability of these substances and their approximate limits of composition.

*Other Reactions leading to the Formation of Photo-chloride.*

A few more instances are here added, indicating the variety of ways in which this product may be obtained.

The following is an interesting reaction. If a solution of ferrous sulphate is made strongly acid with HCl and solution of silver nitrate added, the silver is thrown down as white chloride. But if to the silver solution is first added a little ammonia, enough to re-dissolve the oxide, but much less than enough to neutralise the acid added to the iron solution, then, on pouring the silver solution into the iron, the silver falls as red chloride. So obtained it has at first a dull purple or shade, but by purification, as before described, a good product is obtained. This method, however, scarcely tends to the production of the splendid copper red shades of colour that are got by acting on silver chloride dissolved in ammonia with ferrous sulphate and then adding dilute sulphuric acid. The shade of colour shown by any particular specimen is always of interest, because, as before mentioned, it modifies the effect exerted upon it by the spectrum.

*Potassio-ferrous Oxalate.*—The now well-known "oxalate developer" which I described in the *American Journal of Science* some years ago, throws down from silver nitrate a black powder; this precipitate treated with HCl scarcely alters in appearance, but washed and boiled with dilute nitric acid changes to a deep purple.

*Pyrogallol* is capable of leading to the formation of photo-chloride. When ammoniacal solution of silver nitrate is poured into solution of pyrogallol in water made strongly acid with HCl, in such proportion that the mixed solutions remain strongly acid, there falls a greyish product which by washing and treatment with hot dilute nitric acid becomes bright pink.

*Ferrous oxide* differs essentially in its action on silver solutions from ferrous sulphate. A silver nitrate solution added to one of ferrous sulphate precipitates grey metallic silver. But if potash or soda is first added to the ferrous solution and then silver nitrate followed by HCl, the red chloride is formed abundantly. This reaction is similar to that already described in which an ammoniacal solution of a silver is added to one of ferrous sulphate.

To the same class of reactions belongs the following:—Silver carbonate with excess of sodium carbonate is thrown into solution of ferric sulphate, and after standing a few minutes HCl in excess is added. The silver is converted into red chloride.

It seemed possible that silver itself might be made the means of reducing its chloride. The experiment was made in this way:—Freshly precipitated and still moist chloride was intimately mixed with metallic silver in fine powder and a little water. This was heated till the water boiled and nitric acid was added. After the action was over the chloride had assumed a deep pink colour. A similar result is obtained without the aid of heat, but the resulting colour is much paler.

Analogous to this is the following:—When a cake of fused silver chloride in a crucible is reduced with dilute sulphuric acid and zinc, if the reduction is interrupted when not quite finished, and the metallic silver is dissolved out with hot nitric acid, the residue of silver chloride will be found to be pink.

When HCl is brought into contact with Ag together with an oxidising agent such as a bichromate or permanganate, it gives rise to formation of coloured chloride. These I have not specially examined, but there can be little doubt that they are identical in nature with the foregoing. So too when silver in contact with mixed potassium chloride and chlorate is cautiously treated with dilute sulphuric acid.

The reactions above described will serve to show under what a vast variety of conditions the photo-salts are formed. Most of the methods here described represent each a whole class of reactions, all resulting in the same general way, and these classes might doubtless be largely added to. Almost any silver solution brought into contact with almost any reducing agent and then treated with HCl, gives rise to the formation of photo-chloride. Almost any chlorising influence brought to bear on metallic silver has the same result. Or when silver is brought into contact with almost any oxidising agent and HCl, it may be said without exaggeration that the number of reactions that lead to the formation of photo-chloride is much larger than that of those leading to production of normal chloride.

*Reactions of Photo-chloride.*

Exposed to ordinary diffuse light all the bright shades of silver photo-chloride quickly change to purple and purple-black. The darker shades are more slowly influenced.

Mercuric chloride gradually changes it to a dirty white.

Mercuric nitrate dissolves it easily and completely, but apparently with decomposition, as it can only be recovered as white chloride.

Potassic chloride seems to be without effect.

Potassic bromide soon converts it to a dull lilac, which at the end of twelve hours showed no further change.

In contact with potassic iodide the colour instantly changes to blue-grey; this change is produced by a quantity of iodide too small to dissolve even a trace of silver; the filtrate is not darkened by ammonium sulphide. With a larger quantity silver is dissolved abundantly. By acting with renewed iodide solution, the substance continually darkens and diminishes until only a few black points, barely visible, are left.

Treated with dilute solution of potassium chlorate and HCl, the red substance gradually passes to pink, to flesh-colour, and finally to pure white.

The action of heat on the photo-chloride is very curious; its tendency is generally toward redness. Specimens appearing quite black are rendered distinctly purple or chocolate by heating to 212° F. in a drying oven. Often when the substance first separates by addition of HCl, it is pure grey; this grey will often be changed to pink by simply heating to 212°. (This happens when a grey form

* A specimen in this stage and before treatment with nitric acid was found to contain 92·68 per cent of silver, showing it to be a mixture of metallic silver with chloride and sub-chloride.

is produced; if the greyness is due to admixed metallic silver, it is only removed by boiling with nitric acid.)

The somewhat surprising change of colour which is often seen when the crude substance is boiled with nitric acid (sometimes from dull dark grey to crimson) is due to three concurrent actions: that of the mere heat, the removal of the silver, and the breaking up of uncombined subchloride.

It is not possible to dissolve out the normal chloride by a solvent like ammonium chloride from the photochlorides, leaving the subchloride behind. When red chloride is boiled with successive portions of strong solution of ammonium chloride in large excess, the material gradually diminishes until, if the operation is continued long enough, there remains a small residue of a warm grey colour, which consists of metallic silver and dissolves without residue in nitric acid.

If sodic chloride is substituted for ammonium chloride, the same result follows, except that the operation is greatly more tedious. If persevered in until the hot solution no longer removes traces of silver chloride, the residue consists of nothing but metallic silver.

*Action of Light on Normal Silver Chloride.*

When silver chloride precipitated with excess of HCl is exposed to light, it becomes with time very dark. Cold, strong, nitric acid, 1·36 sp. gr., extracts a trace only of silver.

The principal action of light on AgCl (precipitated in presence of excess HCl) consists in the formation of a small quantity of subchloride which enters into combination with the white chloride not acted upon, forming the photochloride, and thus is able to withstand the action of strong nitric acid. At the same time a trace is formed, either of metallic silver or of uncombined subchloride, it is impossible to say which. After a certain very moderate quantity of photochloride is formed, the action of light seems to cease. This cessation has been noted by many observers, perhaps most exactly by Dr. Spencer Newbury.

The nature of the product formed by the continued action of light on silver chloride seems to support the conclusion that the subchloride is combined with the whole of the normal chloride after the manner of lakes rather than in equivalent proportions. If the latter were the case it seems probable that the continued action of light would extend to much greater decomposition than it is found to do.

The action of light in the formation of the so-called latent image will be examined in the second part of this paper.

Photobromide and Photoiodide.

It has been already mentioned that bromine and iodine form with silver combinations in all respects analogous to those of chlorine. A more particular account of the bromine and iodine compounds must wait for a succeeding number of the *American Journal of Science*; here it can only be mentioned that these substances are formed much it the same way as the chlorine compound. They are less stable than it, and consequently the number of reactions that lead to their production is somewhat more limited. Each, however, is formed in a great variety of ways, and with the same ease as the chloride. In colour they are for the most part indistinguishable from it, but exhibit different reactions.

Relations of Photochloride to Heliochromy.

The photochloride was examined both with the spectrum and under coloured glass.

The rose-coloured form of photochloride was that which gave the best effect. In the violet of the spectrum it assumed a pure violet colour, in the blue it acquired a slate blue, in green and yellow a bleaching influence was shown, in the red it remained unchanged. The maximum effect was about the line F, with another maximum at the end of the visible violet, less marked than the one at F.

Under coloured glass the colours obtained were brighter; under two thicknesses of dark ruby glass the red became brighter and richer. Under blue glass some specimens gave a fair blue, others merely grey. Under cobalt a deep blue was easily obtained, and under manganese violet a fine violet, very distinct in shade from the cobalt. Green produced but little effect—yellow was sometimes faintly reproduced, but rarely. But the yellow glass of commerce, even the dark yellow, lets through portions of nearly the whole spectrum, as can readily be seen by testing it with the spectroscope.

The dark purple forms of chloride do not give as good results as the rose and coppery shades. These last have many points of resemblance with the material of Becquerel's films, resemblance of colour, probably of composition, as far as we can judge of the constitution of those films from their origin; they were far too attenuated to admit of analysis; and resemblance in the curious way in which their colour is affected by heat, so that the conclusion seems inevitable that they are at least closely related.

There is certainly here a great and most interesting field for experiment; hardly any two specimens of photochloride give exactly the same results with coloured light, and this suggests great possibilities. There is the very great advantage in this method over any previous, that the material is easily obtained in any desired quantity and in a condition most favourable for experiment.

The action of light on photochloride can be a good deal affected by placing other substances in contact with it. Any substance capable of giving up chlorine seems to influence the action somewhat; ferric chloride often acts favourably, also stannic and cupric chlorides.

Evidently an important point in all heliochromic processes is that as white light must be represented by white in the image, it is an essential condition that white light must exert a bleaching action on the sensitive substance employed. Red chloride does not bleach but darkens in white light, but the property of bleaching, to a very considerable extent, may be conferred on it by certain other chlorides, and particularly by lead chloride and zinc chloride.

This I look upon as very important.

Another matter of interest is exaltation of sensitiveness, and this I find is accomplished in quite a remarkable way by sodium salicylate, the presence of which at least trebles the action of light on these substances. And probably on others.

I am persuaded that in the reactions which have been here described lies the future of heliochromy, and that in some form or other this beautiful red chloride is destined to lead eventually to the reproduction of natural colours.

## METHODS FOR DETERMINING THE RELATIVE STABILITY OF THE ALKYL BROMIDES.*

By IRA REMSEN and H. W. HILLYER.

A careful study of the relative ease with which bromine can be extracted from the alkyl bromides by different reagents would undoubtedly reveal many facts of interest and importance. Unfortunately such a study is extremely difficult, owing to a variety of circumstances. In the first place, the bromides of the lower members of the series are quite volatile, and, if allowed to stand at the ordinary temperature, the quantity of substance under experiment constantly decreases. In the second place, the bromides are not soluble in water, a fact which makes it difficult to apply reagents which are insoluble in alcohol. Again, the method which first suggests itself—viz., reduction by means of nascent hydrogen—is one which it is extremely difficult to apply quantitatively. Notwithstanding these and other obstacles, it was thought desirable to make a preliminary study of the different methods which suggested themselves, with the view of determining which of the

* *American Chemical Journal*, vol. v ii., p. 251.

methods are most promising, and what the general character of the results obtained is. These results cannot lay claim to great accuracy, but, as will be seen, they are interesting as showing the relative stability of the bromides which were investigated. The bromides experimented upon were those at hand,—ethyl bromide, normal and isopropyl bromides, butyl bromide, and amyl bromide (boiling-point 119°).

*Action of Zinc and Sulphuric Acid.*

The first experiments which yielded results of interest were those in which the reducing agent was hydrogen from zinc and sulphuric acid. A solution containing 75 c.c. of equal parts of alcohol of about 94 per cent and of sulphuric acid of about 10 per cent, and a quantity of bromide, such that it contained 200 m.grms. of bromine, was placed in an Erlenmeyer flask of 125 c.c. capacity. The zinc used was the common sheet zinc, cut in pieces of one inch by one-half inch. These were bent in the middle at a right angle, so that, when resting upon the two ends, they would expose as uniform an extent of surface as possible. They were cleaned and slightly etched with dilute sulphuric acid, then washed and placed in the flasks, four in each flask, by means of a platinum wire hook, or, better, a small tapering glass rod, bent at a right angle near the end.

The extent of the reduction was determined by estimating by Volhard's method the quantity of bromine abstracted. It was soon discovered that the nitrate of silver decomposed the bromides to a considerable extent, so that in the later experiments the method used consisted in adding ferric sulphate and a small quantity of sulphocyanate solution, and then titrating to disappearance of colour, thus leaving the nitrate as short a time as possible in contact with the bromide. The titrating solutions were so made that each cubic centimetre was equivalent to 1 m.grm. of bromine.

In this way ethyl, isopropyl, and butyl bromides were first examined. It was found that a larger percentage of alcohol was necessary for the solution of the amyl bromide, so that in a second series, in which isopropyl, amyl, and normal propyl bromides were examined, the solvent was 50 c.c. alcohol and 40 c.c. acid. The figures indicate the total number of milligrammes of bromine abstracted from the bromides. This is true also of all subsequent tables given in this paper. All of the experiments of shorter duration described in this paper were carried on in flasks surrounded by flowing water of 9° or 10° temperature. The flasks in the other experiments were also put in water, but the flow of water was not kept up, so that the temperature varied slightly with the temperature of the laboratory. In the first series of experiments, the results of which are recorded below, the time of action was two and a half hours.

Series I.

| | | |
|---|---|---|
| Experiment 1. | Butyl, 3·9 | Ethyl not measurable. |
| ,, 2. | ,, 3·9 | ,, 0·7 (?). |
| ,, 3. | ,, 3·9 | ,, 6 and 1·2. |
| ,, 4. | ,, 3·3 | Isopropyl, 10·6 and 8·4. |
| ,, 5. | ,, 3·3 | ,, 9·6 and 7·8. |

It will be seen that the five experiments with butyl bromide gave results which agreed fairly well with one another, a fact which shows that the method is worthy of consideration. In the four experiments with ethyl bromide the results varied from a quantity of bromine which was too small to be determined to 1·2 m.grms. Finally, in the case of isopropyl bromide, the quantities of bromine extracted in the four cases varied from 7·8 to 10·6. While these results are not as satisfactory as could be desired, they clearly show the relative ease with which the three bromides experimented upon are decomposed by the reagent used. Leaving out the first experiment with ethyl bromide, it appears that, under the same conditions, hydrogen from zinc and sulphuric acid extracts from four to five times as much bromine from butyl bromide as it does from ethyl bromide, and about three times as much from isopropyl bromide as from butyl bromide.

Series II.

| | | |
|---|---|---|
| Experiment 1. | Isopropyl, 6·7 | Amyl, 3·2 and 3·2. |
| ,, 2. | ,, 5·9 | N. propyl, 0·7 and 0·7. |

The time in these experiments was not as long as in the first series.

The results show that the amyl bromide used is somewhat more easily decomposed than normal butyl bromide, and that normal propyl bromide has approximately the same stability as ethyl bromide. The order of stability towards nascent hydrogen evolved from zinc and sulphuric acid is, beginning with the most stable, ethyl, normal propyl, normal butyl, amyl (from fermentation alcohol), and isopropyl bromide. The most important general statement to which the results lead is that *the bromides of primary alcohols decrease in stability towards zinc and sulphuric acid as we pass from the lower members of the series to the higher.*

The marked instability of isopropyl bromide, as compared with normal propyl bromide, indicates that the secondary bromides are much less stable than the corresponding normal bromides.

Another series of experiments confirmed the results already commented upon, as far as the order of stability is concerned.

*Action of Nascent Hydrogen evolved from an Alkaline Solution.*

Some time ago, at the suggestion of one of us (R.), Mr. E. H. Keiser tried some experiments on the action of sodium amalgam on alcoholic solution of alkyl bromides. The results were later found to be untrustworthy, because the alkali alone was found to decompose the bromides, and, as no allowance had been made for the double action, it was impossible to decide how much of the total action to attribute to the alkali and how much to the hydrogen. The fact that when sodium amalgam is used the quantity of alkali in solution is constantly increasing throughout the experiments, and at a comparatively rapid rate, complicates the conditions of the experiments. Accordingly another method for getting nascent hydrogen from an alkaline solution was desirable, and the following was devised:—

It had been observed that when zinc is put into an ammoniacal solution of cobalt sulphate it soon becomes coated with a firm, glossy coating of cobalt, and that in this condition it gives a fairly good evolution of hydrogen when placed in a solution of caustic soda. The zincs were prepared by placing them in a shallow dish resting on their ends, and covering them with a strongly ammoniacal solution of cobalt sulphate containing 1 or 2 grms. to the litre, and sufficient ammonium sulphate to keep the cobalt in solution as double sulphate. The zincs were allowed to remain in this for a short time, till there was quite a rapid evolution of hydrogen, when the solution was poured off and the zincs washed. They were rendered more active by treating them with very dilute sulphuric acid and washing them a second time with several changes of water.

In the first experiments a large number of zincs were treated at once with the cobalt solution, with the object of making them of equal reducing power. The caustic soda solution was made from sodium by dissolving about 65 grms. of metallic sodium in a litre of alcohol of about 75 per cent.

The solutions, when in action, contain 30 c.c. alcohol, 20 c.c. water, 10 c.c. caustic soda solution, and a quantity of bromide containing 200 m.grms. of bromine. The soda solution was added, by means of a pipette, as rapidly as possible to the different flasks making up a series for comparison. At the end of the action the zincs were removed in the order in which they had been introduced,

thus securing a very nearly equal time for the action of the zincs in each flask. An equal quantity of nitric acid was then added to each flask, sufficient to neutralise the alkali. In order to have a control of the rate of action in each series there was one flask with ethyl bromide and no zincs and one with ethyl bromide and four zincs. Parallel with these was run a series containing eight other flasks with some other bromide, four with four zincs each, and four without zincs, with the object of determining the action due to the hydrogen, by subtracting from the total amount of bromine extracted the quantity extracted by the alkali alone in the flasks without zincs. The action continued for about sixteen hours.

*First Day's Experiments.*

| | With Zn. | Without Zn. | Difference. |
|---|---|---|---|
| Ethyl .. .. | 46·2 | 28·7 | 17·5 |
| Amyl .. .. | 17·8 | 4·9 | |
| ,, .. .. | 19·9 | 4·2 | |
| ,, .. .. | 19·2 | 4·5 | |
| ,, .. .. | 19·9 | 4·9 | |
| Mean .. | 19·2 | 4 6 | 14·6 |

*Second Day's Experiments.*

| | With Zn. | Without Zn. | Difference. |
|---|---|---|---|
| Ethyl .. .. | 44·1 | 26·6 | 17·5 |
| Butyl .. .. | 12·4 | 3·4 | |
| ,, .. .. | 12·4 | 3·1 | |
| ,, .. .. | 11·9 | 3·4 | |
| ,, .. .. | 12·9 | 3·4 | |
| Mean .. | 12·4 | 3·3 | 9·1 |

*Third Day's Experiments.*

| | With Zn. | Without Zn. | Difference. |
|---|---|---|---|
| Ethyl .. .. | 42·0 | 26·4 | 15·6 |
| Isopropyl .. | 13·7 | 3·5 | |
| ,, .. | 13·5 | 3·3 | |
| ,, .. | 14·0 | | |
| ,, .. | 13·7 | | |
| Mean .. | 13·7 | 3·4 | 10·3 |

As the quantity of bromine extracted from ethyl bromide in the third day's experiments is smaller than in the experiments of the first and second days, it is probable that the figure for isopropyl bromide does not truly represent its stability as compared with the bromides used in the experiments of the first and second days. The proportion 15·6 : 17·5 :: 10·3 : $x$ ought to give a figure comparable with the 14·6 obtained for amyl bromide and 9·1 obtained for butyl bromide.

Two series of observations were now carried on, each series including ethyl, normal propyl, isopropyl, butyl, and amyl bromides. The results obtained in each series are comparable with one another, but the results obtained in Series I. are not comparable with those obtained in Series II., as the conditions were not exactly the same in the two.

| | Series I. | Series II. | |
|---|---|---|---|
| Ethyl .. .. | 40·9 | 54·2 | with zincs. |
| ,, .. .. | 28·0 | 35·7 | without zincs. |
| ,, .. .. | 12·9 | 18·5 | difference. |
| N. propyl .. | 24·5 | 32·2 | with zincs. |
| ,, .. | 9·8 | 11·9 | without zincs. |
| ,, .. | 14·7 | 20·3 | difference. |
| Isopropyl .. | 11·5 | 16·4 | with zincs. |
| ,, .. | 5·6 | 4·9 | without zincs. |
| ,, .. | 5 9 | 11·5 | difference. |
| Butyl .. .. | 11·2 | 12·6 | with zincs. |
| ,, .. .. | 3·5 | 3·8 | without zincs. |
| ,, .. .. | 7·7 | 8·8 | difference. |
| Amyl .. .. | 16·8 | 18·5 | with zincs. |
| ,, .. .. | 4·5 | 5·6 | without zincs. |
| ,, .. .. | 12·3 | 12·9 | difference. |

These results, as well as those on preceding column, show at least that, whether we consider the total action of the alkali and the hydrogen, the action of the hydrogen alone as shown by the differences, or the action of the alkali alone, the order of stability is entirely different in these experiments from that obtained in the experiments with zinc and sulphuric acid. *In acid solution ethyl and normal propyl bromides are most stable, and isopropyl bromide least so. In alkaline solutions, on the contrary, the reverse is true; that is to say, ethyl and normal propyl bromides are least stable, and isopropyl bromide is, of these three, the most stable.* The results are less striking as far as butyl and amyl bromides are concerned. These bromides appear to have about the same stability towards alkali alone as isopropyl bromide, very much greater than ethyl bromide. On the other hand, the presence of the zincs increases the decomposition to about the same extent in the case of amyl bromide as in that of ethyl bromide, while in the case of butyl bromide the increase is somewhat less.

(To be continued).

# PROCEEDINGS OF SOCIETIES.

## PHYSICAL SOCIETY.

*June 11th*, 1887.

Shelford Bidwell, F.R.S., Vice-President, in the Chair.

A number of Puluj and other vacuum tubes were exhibited by Dr. Warren de la Rue. The Puluj tubes consisted of a phosphorescent lamp, and radiometers with phosphorescent vanes, and mica discs painted with phosphorescent substances. The other tubes contained different phosphorescent minerals, such as magnesium carbonate, calcium silicate, and Iceland spar. When illumined by a large induction-coil beautiful colour effects were produced.

The following papers were then read:—

"*Note on Beams Fixed at the Ends.*" By Profs. Ayrton and Perry.

This paper contains a simple method of solving problems relating to horizontal beams with vertical loads, and fixed at both ends. The curve of bending moment for the given distribution of load is first plotted supposing the beam "*supported*" at the ends; and the constant by which the ordinates of this curve exceed those of the true curve, is determined from the condition that the angle between the end sections must be nought. If M is the bending moment at a section, I the moment of inertia of the section about its neutral line, and E Young's modulus of elasticity for the material, then—

$$\frac{M}{E\,I}$$

is the curvature of the beam at that section. If o o′ is a short length of the beam, the angle between the originally parallel sections at o and o′ is—

$$\frac{M}{E\,I}.\,o\,o'.$$

Hence if the beam be divided into a great number of parts, and the values of M and I determined at the middle of each, then—

$$\Sigma \frac{M}{I} . o o' = o \quad . \quad . \quad . \quad (1)$$

since E is supposed constant. But $M = m - c$, where $m$ is the bending moment at the same section, supposing the ends "supported."

$$\therefore \Sigma \frac{m-c}{I} = o; \qquad \text{or } \Sigma \frac{m}{I} = \Sigma \frac{c}{I} .$$

$$\therefore c = \frac{\Sigma \frac{m}{I}}{\Sigma \frac{1}{I}} \quad . \quad . \quad . \quad . \quad (2)$$

The following rule results:—Knowing $m$ and I at every point, divide the beam into any number $n$ of equal parts, find $\frac{m}{I}$ at the middle of each part, and take their sum; this gives the numerator of (2). Find $\frac{1}{I}$ at the middle of each part; their sum gives the denominator of (2). From this $c$ is determined. Diminish all the ordinates of the $m$ diagram by $c$, and we have the diagram of bending moment for a beam fixed at both ends, with any assumed distribution of load and variation of cross section. Particular cases are worked out in full. Numerous drawings made by students of Finsbury Technical College were exhibited, showing applications of the method to different distributions of loading.

"*Note on Messrs. Vaschy and Touanne's Method of Comparing Mutual Induction with Capacity.* By Prof. G. C. Foster.

In November last the author described a method of compairing the mutual induction of two coils with the capacity of a condenser. Since then he has found that a very similar method was used by Messrs. Vaschy and Touanne, in July, 1886, and published in the *Electrician* the following month. The formulæ are identical, and the difference consists in interchanging the galvanometer and the variable resistance $p$. Messrs. Vaschy and Touanne's arrangement has the advantage that the resistance of the secondary coil need not be known. Prof. Foster's method had been used by one of his students (Mr. Draper) about two years ago, but priority in publication belongs to Messrs. Vaschy and Touanne.

Prof. Perry asked the meeting for suggestions to explain why a strip of steel twisted about its longitudinal axis at a red heat, and allowed to cool, tends to untwist when under tension; and for a formula to calculate the amount.

"A Note on Magnetic Resistance," by Profs. Ayrton and Perry, was postponed.

## NOTICES OF BOOKS.

*Report on the Purity of Ice from Onondaga Lake, the Erie Canal, and Cazenovia Lake.* By J. T. Gardiner.

It is a matter of common belief that water, while freezing, purifies itself. This is true to a certain extent, but how the idea should have become so general is difficult to say; possibly it has been deduced from the statements made by Arctic travellers, of melting the sea ice and being able to drink the water. This is accounted for in the following manner:—Salt water freezes at a lower temperature than fresh water, and at the same time loses some of its salt; after passing through the winter, the first warm rays of the sun raise the temperature very gradually, but sufficient for some of the brine to run off, leaving purer ice behind. Thus, after several successive summers and winters, the ice becomes sufficiently free from salt as to be drinkable when thawed; this explanation is borne out by the fact that it is always *old* ice which is used for procuring potable water.

Mr. Gardiner's examination of the ice from the districts herein mentioned was made for the purpose of proving whether or not organic impurities existing in the water were contained in the ice procured from that water, and it was found that, though it might free itself from some, yet it cannot get rid of all, and it is proved that ice always contains at least 10 per cent of the organic impurities in solution.

Besides retaining dissolved organic matter, ice also harbours bacteria, and Prof. Kendrick has found that −120° F. is not sufficient to destroy the germs of disease, and living organisms. The condition of Onandaga creek is such, that it is surprising that severe epidemics of disease are not of constant occurrence. The flow of the stream in summer falls as low as 10,000,000 gals. per diem, and yet some 5,000,000 gals. of sewage are daily poured into it; this stream of filth is one of the principal sources from which the lake is supplied, so the ice thence obtained has been very properly condemned.

The other places whence ice was obtained were examined, and though neither were so bad as that from Onandaga lake, still that from the Erie canal was condemned, as it appeared that better ice could easily be obtained from other places.

*Easy Methods for the Examination of Milk.* By Dr. Paul Vieth. The Aylesbury Dairy Co. 1887.

The writer of this pamphlet states that his intention here is only to put before the public in an easy manner methods of testing milk which are at the same time useful and reliable, and that this must not be considered as a treatise on the subject. On looking through the pages it is evident that he has succeeded in his object. He first describes the use and method of using lactometers, and the combined lactothermometer by which the specific gravity and the temperature of milk can be taken simultaneously by the same instrument. The unsatisfactory and often tedious method of estimating the quantity of cream in milk by "setting" is being gradually replaced by the ingenious machine known as the control centrifugal apparatus, in which 54 samples can be tested in fifty minutes; a similar machine used for separating the cream, called a lactocrit, is also used in some dairies. Both of these instruments are fully described and illustrated. Very extensive series of experiments have proved that the results obtained are in perfect agreement with those of the best gravimetric methods, while the saving of time is very considerable.

It was for a long time thought that the opacity of milk might be taken as a measure of the fat globules contained in it, and lactoscopes have been constructed for this purpose; but as the serum in which the fat floats is itself opaque, and likewise varies in opacity in different samples, it is not surprising that these instruments have, owing to being based on a wrong principle, failed to give satisfaction. The method of using Soxhlet's areometric process is fully gone into; much more correct determinations can be obtained by its means than by the lactobutyrometer.

At the end we find a table of corrections for temperature in taking the specific gravity, one for estimating the results obtained by the use of the areometer, the same for the butyrometer, and others.

Dangers of the Use of Whey and Cheese from the Milk of Tuberculous Cows.—V. Galtier.—The author has demonstrated by numerous and varied experiments the dangerous character of such products. Poultry and swine may also contract phthisis if fed upon dairy produce of this character, and their flesh may then, in turn, impart the disease to man.—*Comptes Rendus*, Vol. civ., No. 19.

## CORRESPONDENCE.

### THE INSTITUTE OF CHEMISTRY.

*To the Editor of the Chemical News.*

SIR,—I have been unable till now to reply to Mr. H. M. Carrington's note in the CHEMICAL NEWS (vol. lv., p. 212), relative to the questions which were under discussion in your Journal some time ago. I may say that these questions are now receiving the serious consideration of the Council.—I am, &c.,

WILLIAM THOMSON.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 19, May 9, 1887.

**Fluctuations of Phosphoric Acid in Cow's Milk.**—A. Andouard.—Phosphoric acid diminishes in milk from the beginning to the end of lactation. The butter, and especially the sugar, diminish likewise in quantity during the same interval. Of four cows, two gave an increasing and two a decreasing proportion of caseine. The increase of the solids of milk in the course of lactation is therefore not an invariable fact. The age of the cows under observation has only seemed to affect the quantity of the milk, the youngest having produced the least. The nutritive value of the food has evidently improved both the quantity and the quality of the milk. Contrary to the assertion of Kræmer, green forage is preferable to dry forage for milch-cows. The best green forages in Western France are by far cabbages and leguminous plants. Then follow in the order of merit potatoes, beet-root, and maize. Individuality appears to be the most important factor among those which modify the quantity and the composition of milk.

**Influence of Materials Employed in the Construction of a Well on the Composition of the Mineral Water of Montrond.**—M. Terreil.—In January, 1886, the author received for analysis a sample of mineral water from a recent bore-well at Montrond. It was found alkaline from caustic soda and lime without a trace of carbonic acid. After the lapse of twelve months the water was found to contain only one-fourth of its soda in the caustic state, the rest being carbonated; it further contained not a trace of lime. The author insists on the necessity of great care in sampling newly discovered waters.

No. 20, May 16, 1887.

**Contribution to the Study of the Alkaloids.**—Oechsner de Coninck.—The author examines the action of methyl iodide upon nicotine. On adding hydrochloric acid in excess to the alcoholic solution obtained, and pouring the whole into a large quantity of water, there appears a splendid green fluorescence, reminding the observer of fluoresceine. By transmitted light the liquid is orange, but by reflected light an intense green. The alcoholic solution, if acidified, colours silk and wool a yellow very similar to that of picric acid. But the fibre is not dyed, as the colour can be entirely removed by washing in water.

**Action of Acetylene upon Benzene in Presence of Aluminium Chloride.**—Raoul Varet and G. Vienne.—On causing acetylene to react upon benzene in presence of aluminium chloride, two successive reactions take place. The first yields cinnamene and the second diphenylethane and dibenzyle, which are isomers. Neither naphthalene hydride nor carbide are produced.

*Justus Liebig's Annalen der Chemie,* Vol. ccxxxviii., Parts 1 and 2.

**Condensation-Products of Acetone and Acetophenone with Aniline and Ammonia.**—P. Riehm.—The following are the principal results laid down in this memoir. Between ketones which contain a methyl attached to the CO and the aldehyds, there has been shown a further analogy in behaviour. That is, it has been shown that one $CH_3$ of the ketones can be split off just as the H-atom of the aldehyds. On the action of acetone upon aniline there is formed:—(1) An $\alpha$-$\gamma$-dimethyl-chinoline with elimination of water and methane. (2) A tertiary base—

$$C_6H_5N = C\begin{matrix}CH_3\\CH_3\end{matrix}$$

with elimination of water. On the action of acetophenone upon aniline there is formed a crystalline base, boiling about 340°. It yields crystalline salts, which have not yet been closely examined. On the action of acetone upon ammonium chloride there is formed, at very high temperatures, $\beta$ collidine, with abscission of water and methane. On the action of acetone upon urea there are formed, at temperatures between 110° and 140°, $\beta$-collidine and a characteristic base, probably $C_{16}H_{19}N$. The substance formed on the action of acetophenone upon ammonia, *i.e.*, acetophenonine, has the empirical formula $C_{23}H_{17}N$, and must be regarded as triphenylpyridin.

**Communications from the Chemical Institute of the University of Bonn.**—These consist of a memoir by O. Wallach on the terpenes and ethereal oils, and one by E. Weber on the ethereal oils.

**Researches on Gold.**—Gerhard Krüss.—In this second paper the author submits previous determinations of the atomic weight of gold to an experimental criticism, especially as the results obtained vary considerably for each other. As a preparatory step to the re-determination of the atomic weight, he discusses the preparation of absolutely pure gold, for which he proposes three methods. He then examines the spark spectrum of gold and the influence of temperature upon spectral-analytical methods and determinations. This section will be reproduced at some length at the earliest possible opportunity. The last portion of this memoir, on the quantitative determination of gold, and its separation from the platinum metals, will also be given at length.

**Synthetic Experiments with Acetacetic Ester.**—L. Knorr.—A voluminous memoir, which does not admit of useful abstraction.

**On Lactucerine.**—Dr. G. Kassner.—The author obtains lactucerine from a residue of lactucarium, which is insoluble in benzine. This residue contains both caoutchouc and lactucerine.

**The Alkaloids of Jaborandi Leaves.**—Erich Harnach.—In addition to pilocarpine and jaborine, previously recognised, the author finds a well characterised base, pilocarpidine, which is capable of conversion into jaboridine.

## MISCELLANEOUS.

**Friedrich's New Mercury Pump.**—There are at present two distinct systems of mercury pumps in use, viz., the Giessler and the Sprengel; the Sprengel is well known as giving a much higher vacuum than it is possible to obtain with any other pump, but its action is too slow when large receivers have to be exhausted. The Giessler pump and its various modifications are much quicker in their action, but they all have some drawbacks, such as a number of stopcocks, or long fragile tubes which are

liable to get broken. Friedrich's new pump is on the Geissler system, and though it does not claim to remove all the disadvantages possessed by the others, yet it succeeds, by means of a novel stopcock, in effecting several improvements and simplifying the manipulation. The stopcock referred to is a three-way one, but instead of the two borings going straight through the stopper, they lie oblique to its axis, and thus the gradual formation of the groove between collar and stopper is avoided, and a much more perfect joint secured, a very good vacuum can quickly be obtained, and, owing to its simplicity, the price of this pump is less than that of any similar one, which is another point in its favour.

## MEETINGS FOR THE WEEK.

Wednesday, 22nd.—Geological, 8.
Thursday, 23rd.—Royal Society Club, 6.30. (Anniversary).
Friday, 24th.—Quekett Club, 8.
Saturday, 25th.—Physical, 3. "Note on Magnetic Resistance," by Prof. W. E. Ayrton, F.R.S., and Prof. J. Perry, F.R.S. "On Sounding Coils," by W. Stroud, D.Sc., and J. Wertheimer, B.Sc. "On Comparing Capacities," by W. E. Rimington. "On the Effects of Change of Temperature in Twisting or Untwisting Wires which have Suffered Permanent Torsion," by Herbert Tomlinson. "On Permanent Magnet Ammeters and Voltmeters with Invariable Sensibility," by Prof. W. E. Ayrton, F.R.S., and Prof. J. Perry, F.R.S.


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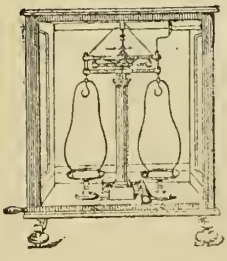

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THE CHEMICAL NEWS.

Vol. LV. No. 1439.

## HER MAJESTY'S JUBILEE.—A SCIENTIFIC RETROSPECT.

### II.

In no department has the progress effected during the last half century been more striking than in chemical analysis. In 1837 we were, practically speaking, confined to what is now known as the gravimetric method. This method has, in itself, been wonderfully developed; reagents are obtained of higher purity, balances and other instruments of a greater precision are now to be procured, and the results arrived at are more closely scrutinised and compared. Above all, possible sources of error have been jealously sought for, and have been found. Thus we now know that substances once deemed absolutely insoluble in water, in cold dilute acids, or in saline solutions, are liable to be appreciably attacked. We find that compounds once supposed to be thrown down from their solutions in a state of perfect purity, in reality entangle or occlude varying quantities of foreign matter, from which they are not always freed without much care and patience.

To take a very familiar instance: how simple seemed the determination of sulphuric acid in a complex saline solution, as described in manuals of the first third part of the century,—so simple that the veriest tyro of a laboratory boy could scarcely be supposed, except by malice aforethought, to come wide of the mark. But if we look over an analytical text-book, written in the light of the present day, we shall see laid down a number of precautions the neglect of which may involve errors in excess or in deficiency, as the case may be.

Along with the desire for increased accuracy there has sprung up a demand for dispatch—we might almost say for hurry—in the completion of an analysis. In pure science this demand is, of course, not felt. But where analyses are executed for technical and commercial purposes speedy execution is desired as much as, if not more than, thorough accuracy. In some technical and commercial establishments it is the rule that, however many samples are sent into the laboratory in the morning,—perhaps not at a very early honr,—the results must be handed in to the office before closing time. Indeed a well-known writer considers it "not surprising that the energies of scientific men have been taxed to devise new and rapid methods of chemical analysis to meet the wants of these high-pressure times." It is, of course, not the place to examine whether, having the game in their own hands, they might not better have pursued a different policy.

Another consequence—though it might have occurred independently—has been the development of volumetric analysis. Alkalimetry and acidimetry were, of course, known at an earlier date, but the extension of the principle to the majority of inorganic and some organic matters of commercial value falls well within the Victorian era. The entire volumetric method has been in some quarters brought into unmerited discredit by the mistakes of its earlier advocates, who, feeling satisfied that they had here processes which enabled them to dispense with tedious or delicate separations, often overlooked the influence of foreign bodies altogether. Thus in determining copper in ores and slags, by the well-known method of Parkes, the presence of cobalt, nickel, manganese, &c., was too often ignored. That we have now certain volumetric processes which are fairly comparable with the best gravimetric determinations, as far as accuracy is concerned, is a fact which needs no demonstration.

Colorimetry, a branch of volumetry, has grown into practical importance in the half century, in the hands of such chemists as Eggertz and Carnelley.

But we have a decidedly novel and plainly modern development of volumetry in gas analysis. The eudiometer was of course known and used in the last century, by Cavendish and others. But the systematic determination of a complex gaseous mixture is a thing of to-day. Without it we could have no useful knowledge of the gases within the lead-chambers or at different points of the blast-furnace. Thus the manufactures of sulphuric acid and of iron—the one the initial point of our chemical, and the other of our mechanical industries—are unspeakably indebted to volumetric gas analysis. Little less striking is its advantage in sanitary chemistry.

An entirely new departure belonging to the era in question is spectroscopic analysis, qualitative and quantitative. That infinitesimal quantities of certain methods can be detected by means of the spectroscope and its accessories,—*e. g.*, sodium even to the 1,400,000th of a m.grm.—is fully established.

Most of the rare earths are readily distinguished from each other by means of their spectra, a process which has the advantage of requiring merely an infinitesimal portion of material. But much remains to be done before the spectroscope becomes of general utility in quantitative research. Prof. Chandler Roberts has not found its indications useful for the assay of alloys of the precious metals, the great obstacle being the difficulty—we might say the impossibility—of obtaining indications fairly representative of the whole ingot.

Another great step has been the introduction of electrolytic analysis. In this manner many metals can be determined with remarkable dispatch, accuracy, and simplicity. In electrolytic methods the number of operations and the reagents used are minimised, and consequently the possibilities of error are reduced in a like proportion. As an excellent specimen of an electrolytic process we may mention the Mansfeld copper-assay. It becomes at least conceivable that even certain organic compounds may be separated from foreign matter by electric action, and isolated in a ponderable state. But this is a task which must be left for the next half century.

Blowpipe analysis has been very extensively developed in the hands of a number of chemists and mineralogists, of whom Plattner, Chapman, and Ross may perhaps be fairly singled out. The epoch-making feature here must be pronounced the applications of the blowpipe in quantitative determinations,—an innovation which will doubtless do much to restrict the field for furnace assays. That the Cornish copper-assay should have survived so long is a singular feature in the history of applied science. As far as gold and—to some extent—silver are concerned, cupellation still reigns supreme.

As one of the novelties of the Victorian era, and as one in which Britain has had the largest share, we must mention the analysis of waters, both for domestic and for industrial uses, as well as that of sewage and waste waters. In this department the name of Clarke stands prominent for the practical determination of hardness, whilst those of Frankland, Wanklyn, Tidy, and Leeds will be remembered for having rendered the estimation of organic dissolved matter possible, at least, with an approximate degree of accuracy.

If we may, in concluding this part of our subject, venture on a suggestion, we would point out that the human organs of scent are—according to the researches of Fischer and Penzoldt—capable of detecting certain substances with a degree of delicacy 250 times greater than that of the eye by means of the spectroscope. On the other hand, we know from our own experience, and from the testimony of friends, that odours, even in the absence of a scientific nomenclature, fix themselves in the memory far more vividly and tenaciously than do colours, forms, sounds, or even words. Perhaps there is here the germ of a new analytical method.

## THE AIR OF SEWERS.*

By Professor CARNELLEY, D.Sc., and J. S. HALDANE, M.A., M.B., University College, Dundee.

OWING to the complaints which had been made of bad smells in the House of Commons a Select Committee was appointed in the spring of 1886 to inquire into the ventilation of the House. By that Committee the authors were instructed to make a series of analyses of the air in the sewers under the Houses of Parliament, and to report thereon. Since then they have examined a considerable number of sewers in Dundee, and have also made a number of laboratory experiments. The object of the research was to obtain a general idea of the amount of some of the more important impurities in sewer air, and to throw some light on their sources, and the conditions affecting their dissemination.

After giving a brief *résumé* of the results of the analyses which had been previously made of sewer air, the authors describe the methods they have employed, and the nature and condition of the sewers they have themselves examined.

As a result of their investigation they found—(1.) That the air of the sewers examined was in a much better condition than might have been expected. (2.) That the carbonic acid was about twice, and the organic matter rather over three times as great as in outside air at the same time, whereas the number of micro-organisms was less. (3.) That in reference to the *quantity* of the three constituents named the air of the sewers was in a very much better condition than that of naturally ventilated schools, and that with the notable exception of organic matter it had likewise the advantage of mechanically ventilated schools (*cf.* paper by the authors and Dr. Anderson in *Phil. Trans.*, 1887). (4.) That the sewer air contained a much smaller number of micro-organisms than the air of any class of house, and that the carbonic acid was rather greater than in the air of houses of four rooms and upwards, but less than in two- and one-roomed houses. As regards organic matter, however, the sewer air was only slightly better than the air of one-roomed houses, and much worse than that of other classes of houses. (The data for all the classes of houses refer to sleeping rooms when occupied during the night.)

The amount of carbonic acid found by the authors was much less than that noted by earlier observers, showing that the sewers they examined were much better ventilated than those previously investigated.

On taking the average of a comparatively large number of analyses it was found that the quantity of organic matter in sewer air increased with the carbonic acid, whereas the micro-organisms on the whole decreased with increase of the other constituents.

With regard to the sources of the several impurities in sewer air the following conclusions are drawn:—(1.) The *carbonic acid* in excess of outside air may be partly due to diffusion from the neighbouring soil, but its chief source is probably the oxidation of the organic matter in the sewage and in the air of the sewer. (2.) The *organic matter* in excess of outside air is most probably wholly or for the most part gaseous, and is of course derived from the sewage itself. (3.) The *micro-organisms* in sewer air come entirely, or nearly so, from the outside, and are not derived, or only in relatively small numbers, from the sewer itself. This is proved by the following facts:—*First*, the average number of micro-organisms in sewer air was less than in outside air at the same time—viz., about 9 in the former to 16 in the latter. *Second*, the number increased with the efficiency of the ventilation. *Third*, the average proportion of moulds to bacteria in sewer air was almost exactly the same as in outside air at the same time, whereas one would expect the proportion to be very different were the outside air not the source from which they were derived, seeing that such a difference has been proved to exist in the air of houses, schools, &c. *Fourth*, the naked eye appearance of the colonies from sewer air is similar to that of those from ordinary air. *Fifth*, the state of filthiness of a sewer seems to have no perceptible effect on the number of micro-organisms. *Sixth*, the view that the micro-organisms in sewer air chiefly come from outside is in perfect agreement with what is known as to the distribution of bacteria in air. *Seventh*, results obtained in the laboratory with an experimental sewer prove that the micro-organisms present in air are diminished to nearly one-half in passing along a moist tube 5 feet long and 1¾ inches in diameter at a rate of nearly 1 foot per second, Although most of the micro-organisms in sewer air come from outside, yet there was distinct evidence of their occasional dissemination from the sewage itself. This is the case when splashing occurs, owing to drains entering the sewer at points high up in the roof. It is, therefore, of great importance that drains should be so arranged as to avoid splashing as much as possible.

In view of the fact that ordinary sewer air is to all appearance comparatively innocent as regards its micro-organisms, experiments were also made to see whether it contained any poisonous volatile base of the nature of a ptomaine. These experiments so far as they went had negative results.

Experiments as to the efficacy of ordinary water traps in preventing the escape of sewer gas into houses confirmed and extended the results previously obtained by Fergus.

Though the authors do not discuss the effect of the inhalation of sewer air on health, yet the results of the above investigation are clearly such as to make one much more suspicious as to supposed evidence of the bad effects of ordinary sewer air (at least when not vitiated by splashing), such as that examined by them.

* Abstract of a Paper read before the Royal Society, June 16, 1887.

## ON DIAMIDE (HYDRAZINE) ($N_2H_4$).

By THEODOR CURTIUS.

BY treating diazoacetate of ethyl with a hot concentrated solution of caustic potash, the potassium salt of a new diazo-acid of the fatty series is produced, crystallising in large yellow prisms. This salt differs from other diazo-compounds of the fatty group by not evolving nitrogen on addition of an acid to its aqueous solution, and by separating out unchanged in glittering yellow plates. I am still engaged, along with J. Laing, in investigating this interesting body. I wish here, however, to direct attention to the remarkable change produced when it is heated with dilute sulphuric acid. The yellow colour disappears, no nitrogen being evolved, and, on cooling, fine colourless crystals separate.

These crystals are the sulphate of the long sought for base, diamide; owing to the sparing solubility of this salt in cold water, it is easily obtained pure. Its formula is $N_2H_4.H_2SO_4$.

The hydrochloride, $N_2H_4.2HCl$, is prepared from the sulphate by addition of barium chloride. It is easily soluble in cold water, but sparingly in hot alcohol. Both these salts decompose suddenly when heated. The sulphate is partly reduced with separation of sulphur. The hydrochloride does not form a double salt with platinic chloride.

Free diamide may be obtained by heating its salts with alkalies. It is a gas which, when mixed with much air, has little smell; but concentrated, it attacks nose and throat, yet has little resemblance to ammonia. It is easily soluble in water, turns red litmus blue, and when not too dilute, forms clouds with aqueous hydrochloric acid.

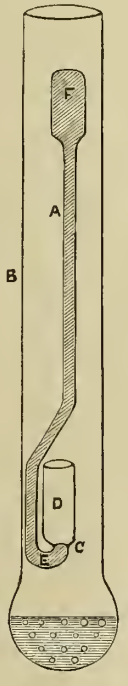
It is a powerful reducing agent, at once decomposing Fehling's solution and ammoniacal silver nitrate. With neutral copper sulphate it gives a red precipitate; the hydrate is precipitated from salts of aluminium, and with mercuric chloride it produces a white precipitate. With

aromatic aldehyds and ketones sparingly soluble crystalline bodies are formed. The solutions of its salts evolve nitrogen on treatment with nitrous acid.

## AN APPARATUS FOR DETERMINING VAPOUR DENSITIES.

By D. S. MACNAIR, F.C.S., A.I.C.,
Lecturer on Chemistry in Allan Glen's Institution, Glasgow.

Of all the methods of determining vapour densities which have come into general use, that of Hofmann is the only one in which the substance is volatilised under diminished pressure. This method, as is well known, has great advantages over all others, especially in the case of unstable bodies, which would decompose at the temperatures required to vapourise them under the ordinary atmospheric pressure. Unfortunately Hofmann's apparatus is somewhat complex and expensive, and for this reason his




method is now but little used. The apparatus which I have devised, and which is shown in the sketch, is essentially a modification of Hofmann's, and will, I think, be found to combine most of its advantages, including at least equal accuracy, with the addition of great simplicity. The apparatus consists of two parts—(1) a syphon barometer tube, A, and (2) an outer tube, B, as in V. Meyer's apparatus. The tube, A, is filled with mercury to the point C. The weighed quantity of substance (20 to 100 m.grms.) in a small stoppered tube is introduced into D, and then, by means of a bent glass rod, is pushed under the surface of the mercury and round the bend, E, whence it rises, through A, into the widened part, F. The tube, A, is now suspended by a wire in the outer tube, B, and the liquid in B (which may be water or any other liquid of known and constant boiling-point) is heated. It is well to loosely close the mouth of B with a cork to prevent the access of air. The liquid in F is soon converted into vapour, and the mercury falls. As soon as its level becomes constant, the difference in level between the mercury in the two limbs of A is read off, best by means of a pendulum cathetometer. The other data required are (1) the barometric pressure, (2) the boiling-point of the liquid used in B, (3) the volume of the vapour in A. The last may be got in various ways; in my own experiments I used an india-rubber ring which could be moved up or down the narrow part of A by means of a bent wire. This being brought to the level of the mercury, the volume of the vapour was found, after cooling, by filling A with mercury to the height of the ring, and then weighing or measuring the mercury. The vapour density is then calculated exactly as in Hofmann's method. I give the details of an actual experiment—

Vapour density of toluene (b. p., 111°) in steam.

| | | |
|---|---|---|
| Weight of substance used .. .. .. .. | 0·0262 | grm. |
| Height of mercury column (at 100°) .. | 428 | m.m. |
| Barometer (at 20°) .. .. .. .. .. | 750·5 | ,, |
| Volume of vapour .. .. .. .. .. | 20·0 | c.c. |
| Vapour density found .. .. .. .. | 46·3 | ,, |
| ,, ,, calculated .. .. .. | 46·0 | |

I hope to be able to publish fuller particulars of the method in a few weeks, after I have had time to test it more thoroughly.

## FLUORIDE OF NITROGEN.

By H. N. WARREN, Research Analyst.

The supposed compound was formed by passing an electric current from seven ferric chloride batteries through a concentrated solution of ammonium fluoride. After the lapse of a short time several drops, of oily consistence, were observed attached to the negative plate. On becoming connected with the positive, a thin gold wire, these drops exploded with great violence. The compound is undoubtedly highly unstable, being at once decomposed in contact with glass, silica, or organic matter, thus rendering the analysis of the same one of considerable risk. Its explosive violence is even greater than the chloride of nitrogen, and it is also prone to spontaneous decomposition.

## VOLUMETRIC ESTIMATION OF ALUMINA.

By RICHARD GATENBY.

This can be done with great facility when it is contained in caustic soda. Take first the amount of caustic soda present with normal HCl acid and phenol-phthalein as indicator. When the phenol-phthalein is decolorised we have the amount of caustic soda present. Then put into it a few drops of methyl orange solution and again add normal HCl, stirring well (not heating) until a pink colour is obtained which does not vanish by stirring for a few seconds. The number of c.c. of normal HCl required by the second titration equals amount of alumina and alkaline soda salts present. Then add litmus solution, and titrate back with normal caustic soda until a decided blue colour appears.

Each c.c. of normal caustic soda required = 0·0257 of alumina.

A sample of caustic soda bottoms from 70 per cent white caustic soda, called by the trade 68 per cent bottoms, tested as follows :—

| | |
|---|---|
| $Na_2O$ .. .. .. .. .. | 57·1 |
| $H_2O$ .. .. .. .. .. .. | 16·5 |
| $Na_2CO_3$, &c. .. .. .. .. | 2·4 |
| $Al_2O_3$ .. .. .. .. .. | 11·3 |
| Insoluble $Fe_2O_3$, &c. .. .. | 12·5 |
| | 99·8 |

This process is very rapid, and accurate enough for technical use. It is a strange fact that alumina is alkaline to methyl orange, and acid to litmus solution.

5, Petworth Street, Cheetham,
Manchester, June 11, 1887.

## A METHOD OF SEPARATING THE TWO ISOMERIC TOLUIDINE-SULPHONIC ACIDS.

By E. A. SCHNEIDER.

WHILE working with the toluidine-sulphonic acids for the purpose of making the hydrazine-sulphonic acids used in the above experiments, I made the observation that the potassium salt of *p*-toluidine-*m*-sulphonic acid, which is very easily soluble in water, is insoluble in cold caustic potash, while the potassium salt of *p*-toluidine-*o*-sulphonic acid is extremely easily soluble in the same liquid at ordinary temperature. The same is true of the corresponding sodium salts. If it is desired to separate a mixture of the two acids into its components it is only necessary to heat it with concentrated caustic potash until it has all passed into solution. If this solution is allowed to cool slowly, the potassium salt of *p*-toluidine-*m*-sulphonic acid crystallises out in stout needles, which can be easily separated from the mother-liquor by means of a platinum cone and a filter-pump. It is advisable to wash the salt in the funnel with alcohol and then quickly to press it between layers of filter-paper. —*American Chemical Journal*, Vol. viii., p. 4.

## LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1887.

By WILLIAM CROOKES, F.R.S.,

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

and C. MEYMOTT TIDY M.B., F.C.S.,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

*To* THE WATER EXAMINER, *Metropolis Water Act*, 1871.

London, June 4th, 1887.

SIR,—We submit herewith the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

During the past month, despite the prejudicial influence of the stormy weather on the state of the river sources, the general character of the water supplied to the Metropolis has been eminently satisfactory. The proportion of organic matter present in the water—not at any period of the year excessive—has, with the advance of the season, undergone an appreciable diminution. Thus, in the case of the Thames-derived supply, the maximum proportion of organic carbon in any one sample was 0·152 part in 100,000 parts of the water; while the mean proportion for the month was 0·134 part, as against a mean of 0·162 part for the preceding month, and a mean of 0·167 part for the previous four months of the year.

As during last month, several samples of the East London Company's Lea-derived supply were found wanting in freedom from turbidity and tint of ochrey colour, consequent not on imperfect filtration of the water, but on special treatment to which the mains of the Company are now being subjected. The condition of this Company's water, in respect to its degree of freedom from organic matter, was, however, unexceptionable, the mean proportion of organic carbon present being only 0·108 part, with a maximum of but 0·131 part in 100,000 parts of the water.

We are, Sir,
Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

## METHODS FOR DETERMINING THE RELATIVE STABILITY OF THE ALKYL BROMIDES.*

By IRA REMSEN and H. W. HILLYER.

(Concluded from p. 282).

*Action of Ammonia on Normal and Isopropyl Bromides.*

THE marked differences between the stability of propyl bromide and that of isopropyl bromide led to the examination of their conduct towards other reagents than those used in the experiments already described. The first one used was ammonia. Standard solutions were made by dissolving 3·8437 grms. of each bromide in 250 c.c. alcohol. Each c.c. of this solution contained 10 m.grms. of bromine. The substances were weighed in tubes of about 8 by 180 m.m. drawn out to a point. One of these, after a file-scratch was made on it near the point, was placed on the balance-pan in an upright position in a small beaker. After weighing, weights amounting to 3·8437 grms. were added to the other pan, and enough of the bromide was run in, by means of a narrow glass tube drawn to a point and used as a pipette, to bring again to a balance. It is not difficult, after a little practice, to weigh in this manner to within a m.grm. The point of the weighing tube, being thrust into the mouth of a 250 c.c. measuring flask, was broken off by pressing it against the inside of the neck of the flask. After the bromide had run out, the tube was immediately rinsed out by pouring alcohol through it. The flask was then filled to the mark with alcohol, and, after thorough mixing, the contents were transferred to tightly stoppered bottles. To 20 c.c. of each of the solutions, 20 c.c. of aqueous ammonia of 10 per cent were added. At the end of about twenty hours the bromine extracted was found to be, in the case of normal propyl bromide, 25·4 m.grms. in one flask and 29·2 m.grms. in another; in the case of isopropyl bromide, 3·8, 4·2, and 5·0 m.grms. in three flasks.

From these results it is clear that normal propyl bromide is much more rapidly decomposed by ammonia than isopropyl bromide. As shown by the experiments above recorded, caustic soda alone extracted 9·8 and 11·9 m.grms. of bromine from normal propyl bromide, while in parallel experiments it extracted only 5·6 and 4·9 m.grms. of bromine from isopropyl bromide.

*Action of Alcoholic Sodium Hydroxide on the Alky Bromides.*

By way of supplementing the experiments described above, in which the action of sodium hydroxide on the bromides was studied, a more extended series of similar experiments was now undertaken. In each flask there

* *American Chemical Journal*, vol. viii., p. 251.

were placed 20 c.c. bromide solution, containing in all 200 m.grms. of bromine, 10 c.c. alcohol, and 20 c.c. caustic soda solution, made by the action of water on sodium amalgam, and containing about 10 per cent sodium hydroxide.

Of the 200 m.grms. of bromine in each flask the following quantities were extracted :—

| | | |
|---|---|---|
| Ethyl.. .. .. | 165·6 or | 82·8 per cent. |
| ,, .. .. .. | 159·2 | 79·6 |
| N. propyl .. .. | 130·5 | 65·2 |
| I. propyl .. .. | 50·4 | 25·2 |
| Butyl.. .. .. | 31·2 | 15·6 |
| ,, .. .. .. | 32·2 | 16·1 |
| Amyl.. .. .. | 65·8 | 32·9 |
| ,, .. .. .. | 67·6 | 33·8 |

These results confirm those already obtained, and indicate clearly that fairly satisfactory results may be expected by a similar comparison of other alkyl bromides with reference to their stability towards caustic soda. The reaction which takes place with this reagent is in all probability represented by the equation—

$$C_nH_{2n+1}Br + C_2H_5OH + NaOH = C_nH_{2n+1}.O.C_2H_5 + KBr + H_2O.$$

That is, a mixed ether containing ethyl and the radical of the bromide used is formed in each case. In the above experiments the odour of common ether was unmistakable in the flask with ethyl bromide. In the flask with propyl bromide there was also a pleasant odour like that of common ether, and quite different from that of the bromide solution. An experiment was performed in which a larger but unknown quantity of normal propyl bromide was treated with caustic soda and alcohol. After standing a week or two the mixture was made neutral with nitric acid, and subjected to distillation, when a small quantity of a volatile liquid was obtained, which had an odour very much like that of common ether and a density less than that of water. The quantity was so small that the boiling-point could not be determined. Several cases are known* in which mixed ethers have been formed by treating halogen derivatives of the hydrocarbons with alcoholic potash at an elevated temperature, but the reaction has not been supposed to take place as easily as we have found it at the ordinary temperature.

### *Action of Soluble Silver Salts on the Two Propyl Bromides.*

Preliminary experiments having shown that silver nitrate slowly decomposes the bromides, its action on the two propyl bromides was next tried.

Twenty c.c. normal propyl bromide solution, 5 c.c. dilute nitric acid, and 25 c.c. solution of nitrate of silver, containing silver equivalent to 25 m.grms. bromine, were put in a flask and allowed to stand for sixteen hours in a dimly lighted place. At the end of this time there were considerable opalescence and some deposition of silver bromide. By titration it was found that 2·7 m.grms. of bromine had combined with silver. A similar mixture containing isopropyl bromide was found to have deposited a heavy, yellowish white precipitate of silver bromide. On titration it was found that, of the 25 m.grms. of bromine with which the silver added was capable of combining, 24·3 m.grms. were thus combined.

From a solution containing 20 c.c. bromide solution, and 20 c.c. of a neutral solution of silver acetate, capable of precipitating 20·2 m.grms. bromine, 19·2 and 19·2 m.grms. bromine were found precipitated in two parallel experiments with the isobromide, while only 2·5 and 2·5 m.grms. were precipitated in parallel experiments with the normal bromide.

The isopropyl bromide is decomposed much more readily by silver nitrate and by silver acetate than normal propyl bromide. Towards silver salts, therefore, these two bromides act in the same way that they do towards zinc and sulphuric acid.

### *Action of Cobalt Zincs and Acetic Acid on Alkyl Bromides.*

Mixtures were made containing 20 c.c. bromide solution and 10 c.c. acetic acid of ordinary strength. These were allowed to act for two hours and twenty minutes on six cobalt zincs prepared as above described. In the case of the normal bromide 2·0 and 1·9 m.grms. of bromine were set free in two different flasks. In the case of the isobromide the quantities of bromine set free were 8·0 and 8·1 m.grms. By adding sufficient nitric acid all of the red ferric acetate formed by adding the ferric sulphate may be changed to the colourless nitrate, so that the titration by Volhard's method presents no difficulties. The action of the mixture of alcohol and acetic acid on the cobalt zincs gives a very regular evolution of hydrogen, which, though not rapid, may be continued for five or six hours before the zinc acetate begins to crystallise out.

The form of the zincs was now changed to that of a flat spiral, made by winding a strip of zinc one-half inch by 24 inches about a small core, then unwinding and loosening the coil till no two turns were in contact. The coil was placed in a beaker which contained the solution of the bromide to be reduced, and a small glass rod, so bent as to make a support for the coil, thus ensuring free circulation.

In one series of experiments in which the action was kept up for about five hours, the normal bromide yielded 4·5 and 4·8 m.grms. bromine, and the isobromide 20·0 and 20·1 m.grms. bromine.

Finally, a series of experiments was made including the five bromides. For this purpose standard solutions were made containing equivalent weights of the bromides, so that 1 c.c. of each solution contained the same number of m.grms. of bromine, the concentration being the same as that of the propyl bromides—viz., 20 c.c. of each solution containing 200 m.m. of bromine. The conditions as regards quantity of bromide, of alcohol, and of acid, were the same as in the last case. The zincs, however, were different. At the end of five hours titration gave the following results :—

| Bromide. | M.grm. Br set free. I. | II. |
|---|---|---|
| Ethyl .. .. .. | 1·2 | 1·5 |
| N. propyl.. .. .. | 3·3 | 3·3 |
| I. propyl .. .. .. | 10·5 | 11·7 |
| Butyl .. .. .. | 6·0 | 6·0 |
| Amyl.. .. .. .. | 9·0 | 9·9 |

It was afterwards found that, by standing in alcoholic solution alone, butyl and amyl bromides are slightly decomposed, so that the above figures for these bromides are somewhat too large.

As was stated at the beginning of this paper, the object of the investigation was to determine which of the various methods which suggest themselves for the purpose of measuring the relative stability of the alkyl bromides are most likely to yield results of value. It seems that the action of zinc and acids is not capable of giving very reliable results, though the general tendency of the action can easily be determined. The action of zinc in alkaline solution is so complicated by the independent action of the alkali alone that it is of little value. In the same way the action of sodium amalgam is also complicated by the fact that the solution constantly grows more and more alkaline. On the other hand, the action of salts of silver on fairly concentrated solutions of the bromides promises good results, as does also the action of ammonia and of caustic soda alone. It is proposed, as soon as possible, to study the reactions with care, using as large a number of bromides as may be obtainable. Among experiments already performed by others, and having some relation to

* *Annales de Chimie et de Phys.* (3), xii., 302 ; *Jahresbericht*, 1850, 560; *Philosophical Magazine* (4), xiv., 186; *Annalen der Chemie*, xcii. 351; *Journal of* (London) *Chemical Society*, xix., 358.

those described in this paper, the following should be mentioned :—

Wislicenus,* by treating various haloid ethers with the sodium compounds of aceto-acetic ester, ethyl aceto-acetic ester, and malonic ester without external application of heat, found the order of stability of some alkyl bromides and iodides. In the order of increasing stability he placed the compounds experimented upon thus : —Methyl iodide, ethyl iodide, primary propyl iodide, ethyl bromide, primary isobutyl iodide, primary propyl bromide, tertiary butyl bromide. Or, taking the iodides alone :— Methyl, ethyl, primary propyl, isopropyl, isobutyl. This is the same order as that observed in the series of experiments with alcoholic caustic soda.

Jackson† studied the relative stability of certain substituted benzyl bromides. By the action of a solution of sodium acetate in alcohol on the ortho-, meta-, and para-brom-benzyl bromides at 100°, he found that the ortho-bromide is the most stable towards this reagent, the meta next, and the para the least stable.

## THE INDIRECT ESTIMATION OF CHLORINE, BROMINE, AND IODINE BY THE ELECTROLYSIS OF THEIR SILVER SALTS.

### With Experiments on the Convertibility of the Silver Salts by the Action of Alkaline Haloids.

By J. EDWARD WHITFIELD.

In the absence of reliable methods for the direct quantitative separation of bromine and chlorine, it is usual to employ one or other of the methods for the conversion of the mixed silver salts to a common condition.

Both the reduction to silver by hydrogen and the conversion of the bromide to chloride by heating in an atmosphere of chlorine are attended with loss by volatilisation and mechanical transfer, and the possible inaccuracy of both the processes is such that they can scarcely be considered as available for the estimation of small amounts of either constituent in presence of large amounts of the other.

Of all such methods the electrolytic analysis of the mixed and fused silver salts, as proposed by Bolley,‡ and more recently introduced and tested by Kinnicutt,§ is probably the best, though, according to Finkener‖, perfect decomposition is difficult to obtain by this method, and there is danger of volatilisation and partial change of the silver salts in the fusion.

Kinnicutt's test analyses of the fused salts show, for silver chloride and silver bromide each by itself, errors of 0·0006 grm. – to 0·0003 grm.+ on amounts varying from 0·7 grm. to 1·8 grms.; and for the mixed silver chloride and bromide, errors from 0·0010 grm.– to 0·0012 grm.+, with a mean of 0·0006 grm.+ on weights varying from 2 grms. to 2·8 grms.

These figures represent the sum of the errors from the weighing of the fused chloride to the weighing of the deposit of silver, and do not include errors made in the precipitation, filtration, transfer to crucible, and fusion.

A method in which the decomposition of the silver salts may be effected without fusion, and which would at the same time place the errors of filtration, preparation for weighing, and subsequent electrolysis at a minimum, seems to be desirable, and a promising line of investigation was suggested by Luckow's assertion¶ that from the solution of silver chloride in potassium cyanide the silver may be thrown down completely.

Luckow gives no figures excepting a common mean of all determinations by the precipitation from the cyanide solution and the decomposition of the solid chloride on the negative pole of the battery under sulphuric acid, so that the first experiments were made to test the accuracy of the battery process under these conditions.

In experiments (1)-(5) silver chloride was the starting-point. In (1)-(3) the freshly precipitated and carefully washed chloride was dried to a constant weight in a platinum dish, protected from the light, at a temperature of about 150° C., dissolved in potassium cyanide, and electrolysed after the addition of a little sodic hydrate, preliminary analyses having seemed to indicate that the presence of sodic hydrate affected the deposition favourably. In all subsequent experiments ammonia, which was found to be of equal service, was used instead of sodic hydrate.

In experiments (4) and (5) the chloride was converted, previous to electrolysis, into the bromide by solution in potassium cyanide, the addition of potassium bromide and precipitation by sulphuric acid as will be described later, and the precipitate re-dissolved in potassium cyanide, the object being to test the action of the battery upon the cyanide solution of the silver bromide.

| | AgCl taken. | Silver found. | Silver calculated. | Error. |
|---|---|---|---|---|
| (1) | 0·1565 grm. | 0·1177 grm. | 0·1178 grm. | 0·0001 grm. – |
| (2) | 1·3004 | 0·9785 | 0·9787 | 0·0002 – |
| (3) | 2·2657 | 1·7047 | 1·7051 | 0·0004 – |
| (4) | 0·7472 | 0·5618 | 0·5624 | 0·0006 – |
| (5) | 0·2854 | 0·2133 | 0·2147 | 0·0014 – |

These results, as far as they go, are satisfactory. Similar tests upon the electrolysis of silver bromide and silver iodide in the cyanide solution were undertaken, but it was thought advisable to combine, incidentally with the tests of the battery process, an examination of the method recently proposed by Maxwell-Lyte* for the direct conversion of silver chloride to the bromide and thence to the iodide.

Field† was the first to propose a quantitative conversion of silver chloride to the bromide by digesting the former in potassium bromide, and the change of the chloride or bromide to the iodide by the action of potassium iodide upon these salts. This method has been variously criticised and finally abandoned as an accurate process,‡ though, so far as concerns the conversion of the chloride and bromide to the iodide, Siewert§ shows it to be exact.

Maxwell-Lyte's method of proceeding, depending upon identically the same principle which Field attempts to utilise, consists in the solution of the silver haloid salts in potassium cyanide, the addition of potassium bromide, the decomposition of the potassium cyanide by means of sulphuric acid, with the consequent precipitation, and weighing of the silver bromide mixed with the iodide of the original mixture—the resolution of this precipitate in potassium cyanide, the addition of potassium iodide, the decomposition of the cyanide as before, with sulphuric acid, with the formation of a precipitate which is presumably pure silver iodide and to be weighed as such.

To convert the chloride to the bromide Maxwell-Lyte uses a weight of potassium bromide equal to the weight of the silver chloride taken; and to change the bromide to the iodide, a weight of potassium iodide one and a quarter times as great as the original weight of the silver chloride.

In the following experiments these amounts have varied widely, but the proportions of alkaline haloid salts employed are given for each case in the tabular statement.

The starting point was generally freshly precipitated silver chloride, but in the last three cases, pure silver, this being dissolved in nitric acid, precipitated with potassium bromide (two equivalents), and the precipitate dissolved in potassium cyanide, converted into the iodide in the manner described, and weighed, the object of this being to test the convertibility of the silver bromide to silver iodide.

* *Annalen der Chemie*, ccxii., 239.
† *Amer. Chem. Journ.*, iii., 252.
‡ *Dingl. Pol. Jour.*, cli., 46.
§ *American Chemical Journal*, iv., 22.
‖ Rose-Finkener, "Quant Anal.," ii., 621.
¶ *Dingl. Pol. Jour*, clxxviii., 43.

* Chem. News, xxxxix., 3.
† *Jour. Chem. Soc.*, x., 234.
‡ Rose-Finkener, *loc. cit.*
§ *Zeit. für Anal. Chem.*, vii., 469.

| | AgCl taken. | AgBr found. | AgBr calculated. | Error. | | Equivalents of KBr taken. |
|---|---|---|---|---|---|---|
| (6) | 0·3260 grm. | 0·4227 grm. | 0·4270 grm. | 0·0043 grm. | − | 2 |
| (7) | 0·3093 | 0·4023 | 0·4052 | 0·0029 | − | 2 |
| (8) | 1·3801 | 1·8041 | 1·8080 | 0·0039 | − | 2 |
| (9) | 0·2091 | 0·2723 | 0·2739 | 0·0016 | − | 10 |
| (10) | 0·6846 | 0·8909 | 0·8968 | 0·0059 | − | 10 |
| (11) | 1·1625 | 1·5202 | 1·5230 | 0·0028 | − | 20 |
| (12) | 1·1734 | 1·5310 | 1·5372 | 0·0062 | − | 20 |
| (13) | 0·3501 | 0·4553 | 0·4586 | 0·0033 | − | 29 |
| (14) | 0·4178 | 0·5468 | 0·5473 | 0·0005 | − | 29 |

| | AgCl taken. | Silver found. | Silver calcula ed. | Error. | |
|---|---|---|---|---|---|
| (6) | 0·3260 grm. | 0·2443 grm. | 0·2453 grm. | 0·0010 grm. | − |
| (7) | 0·3093 | — | — | — | |
| (8) | 1·3801 | 1·0385 | 1·0386 | 0·0001 | − |
| (9) | 0·2091 | — | — | — | |
| (10) | 0·6846 | 0·5137 | 0·5152 | 0·0015 | − |
| (11) | 1·1625 | — | — | — | |
| (12) | 1·1734 | 0·8829 | 0·8831 | 0·0002 | − |
| (13) | 0·3501 | 0·2634 | 0·2634 | 0·0000 | |
| (14) | 0·4178 | — | — | — | |

| | AgCl taken. | AgI found. | AgI calculated. | Error. | | Equivalents taken of KI. |
|---|---|---|---|---|---|---|
| (15) | 0·6996 grm. | 1·1451 grm. | 1·1456 grm. | 0·0005 grm. | − | 2 |
| (16) | 0·7587 | 1·2429 | 1·2424 | 0·0005 | + | 2 |
| (17) | 0·6710 | 1·0992 | 1·0988 | 0·0004 | + | 10 |
| (18) | 0·2515 | 0·4118 | 0·4118 | 0·0000 | | 10 |
| (19) | 0·6501 | 1·0646 | 1·0646 | 0·0000 | | 10 |

| | AgCl taken. | Silver found. | Silver calculated. | Error. | |
|---|---|---|---|---|---|
| (15) | 0·6996 grm. | 0·5255 grm. | 0·5265 grm. | 0·0010 grm. | − |
| (16) | 0·7587 | 0·5691 | 0·5710 | 0·0019 | − |
| (17) | 0·6710 | 0·5042 | 0·5050 | 0·0008 | − |
| (18) | 0·2515 | 0·1892 | 0·1892 | 0·0000 | |
| (19) | 0·6501 | 0·4892 | 0·4892 | 0·0000 | |

| | Silver taken. Grm. | AgI found. Grm. | AgI calculated. Grm. | Error. Grm. | Equivalents taken of KI. | Silver found. Grm. | Error. Grm. |
|---|---|---|---|---|---|---|---|
| (20) | 0·5418 | 1·1790 | 1·1789 | 0·0001 + | 2 | 0·5417 | 0·0001 − |
| (21) | 0·3750 | 0·8154 | 0·8159 | 0·0005 − | 2 | 0·3746 | 0·0004 − |
| (22) | 0·4078 | 0·8859 | 0·8873 | 0·0012 − | 10 | 0·4077 | 0·0001 − |

In most cases the final precipitate, after weighing, was electrolysed, so as to have a more perfect control upon the results of the conversion process, and at the same time to test the battery method additionally.

The bromide and iodide of silver were precipitated hot from dilute solutions, which were cooled and allowed to stand over night to settle before filtering.

Filtrations were made by the use of the Gooch crucible, with gentle pressure; the silver salts were dried directly over a low Bunsen flame at a temperature far below the melting-point, and dissolved, after weighing, by introducing crucible and asbestos into a strong solution of potassium cyanide, and heating, the time necessary for the solution varying from a few minutes to several hours, according to circumstances.

In some cases traces of reduced silver were found with the asbestos, and were recovered by treating the felt with nitric acid and washing, the filtrate and washings being added to the main solution.

The deposition of silver was made in the platinum dish of 100 c.m.³ capacity, which held the solution, and the current found most suitable was (as Luckow originally recommended*) developed by four Meidinger cells of large size.

With solutions of the volume named and the area of the negative electrode employed, it was found advisable not to attempt to treat more than 2 grms. of the silver salt.

The solution was decanted immediately on the stopping of the current, or better, syphoned off while the battery connections were still unbroken, and washed with distilled water, to prevent the solvent action of the cyanide on the deposit.

From these experiments it appears that the deposition of silver from the cyanide solution of the chloride, bromide, or iodide is exceptionally exact; the tendency of the process, however, is to yield low results, and yet, in spite of the multiplicity of operations through which the original material has been passed in the attempt to settle two questions at once, the deficiency is not very great, being 0·0005 grm. in the mean of eighteen determinations, with a maximum value of 0·0019 grm.

The conversion of silver chloride to silver bromide by the method proposed by Maxwell-Lyte is, like its predecessor, too imperfect to be worthy of trust; but the experiments indicate unmistakably that the change of silver chloride or silver bromide to silver iodide is sufficiently complete to afford the basis of a good analytical method.

The indirect estimation of chlorine and bromine, chlorine and iodine, or bromine and iodine, in presence of one another, may be effected satisfactorily, therefore, by precipitating both together as silver salts, filtering on abestos, washing, drying, at 150° C., weighing, dissolving the residue in potassium cyanide, and either electrolysing the solution to determine the silver or precipitating the silver as iodide, again filtering upon asbestos, washing, drying, and weighing.

In a mixture of all these halogens the iodine is first to be separated by known methods and the chlorine and bromine indirectly estimated as described. — *American Chemical Journal*, Vol. viii., No. 6.

* *Loc. cit.*

## NOTICES OF BOOKS.

*The Artificial Organic Colouring-Matters.* Based upon Six Lectures delivered by Prof. E. Noelting at the "Ecole de Chimie," in Mulhouse. Edited by Dr. Paul Julius. (Die künstlichen organischen Farbstoffe. Unter Zugrundlegung von sechs Vorlesungen gehalten von Prof. Dr. E. Noelting, Director der "Ecole de Chimie" in Mühlhausen, bearbeitet von Dr. Paul Julius). Berlin: R. Gaertner.

We may fitly begin our notice of this useful little work with the announcement that, according to a recent decree, all instruction at the Ecole de Chimie is to be given exclusively in the German language. Dr. Noelting's lectures have already appeared in the *Moniteur Scientifique*, but in the book before us they have been enlarged and in some respects apparently re modelled, though with the consent and co-operation of the lecturer.

The first chapter of this work is devoted to a general account of coal-tar and its more important constituents. The author remarks that coal-tar, once a worthless and troublesome by-product, has become a valued and remunerative article of commerce. But we must not forget that the "whirligig of time" has brought on another change: coal-tar, despite the progress of the colour-industry, is again a drug in the market, so that the managers of gas-works are often glad to burn it under their retorts in partial substitution for coke.

In the second chapter Dr. Noelting discusses the intermediate products,—substances obtained from coal-tar and employed in the manufacture of colours, but not having any tinctorial properties, such as aniline, the toluidines, phenol, resorcine, phthalic acid, &c.

The third chapter gives a very clear summary of Witt's researches on the circumstances of the conversion of aromatic hydrocarbons into true colouring-matters. The author enumerates those radicles to which Witt has given the name of "chromophorous groups," which by their introduction generate chromogenes, and he shows how the latter again are transformed into colouring-matters by means of the halogenous groups, the amidic and the hydroxylic.

There follows a brief account of the process of dyeing. The author inclines to the chemical theory rather than the mechanical, and cites phenomena which tell strongly in favour of the former view.

Thus if a skein of silk is steeped in a solution of the (colourless) rosaniline base, and heat is applied, the skein is dyed as full a red as if a salt of rosaniline had been present. We can only understand this fact if we admit that the rosaniline base unites with the fibre to form a salt, and consequently plays the part of an acid.

Prof. Noelting does not, however, seek to overlook the arguments which may be brought forward against the chemical theory. For the facts that cotton fibre, a substance chemically indifferent, is dyed by curcumine (from turmeric), and by the carthamine (of safflower), no explanation has hitherto been produced.

We cannot help considering that this third chapter will prove priceless to all technical students who wish to devote themselves to the tinctorial arts or to the manufacture of colours. We even know of experienced practical men who might study it with great advantage.

The classification of the colouring-matters adopted rests on the chromophorous groups present in each case. We have thus, 1, the nitro- and nitroso-colours; 2, the azo-class (or, as the French persist in calling them, the azoïc group, a term pre-engaged); 3, the triphenylmethan colouring-matters; 4, the phthaleines; 5, artificial indigo; 6, the anthracenes; 7, the chinoline and acridine colours; 8, the indophenols, indamines, and Lauth's colours; 9, the azines, eurhodines, and saffranines; 10, the indulines and nigrosines; 11, aniline black; and 12, galloflavine, canarine, and cachou de Laval, which form an Appendix

These classes are then described in a series of chapters. We may, perhaps, take justifiable exception to the introduction here of indigo. The artificial product is absolutely identical with natural indigo, and is little more than a curiosity. The author admits, in his historical introduction, that "artificial indigo is not in a position to compete with the natural product, and the probability that it will ever become so is very trifling." That probability, or rather possibility, has since been greatly diminished by the introduction of the new "ammonia process" in some factories in India. Not only is the working simplified, but at Tirhoot an increased yield of some 40 per cent has been obtained. Hence the planter will be able to reduce his prices without loss, and the difficulty which synthetic indigo encounters in competing with the natural product will be greatly increased.

One of the first reflections which suggest themselves to the reader is the number of artificial colouring-matters which have fallen into disuse, partial or entire. As such we notice isopurpuric acid, Victoria orange, aurantia, heliochrysine, amido azobenzol, phosphine, aldehyde green, coralline, azuline, hexaoxymethyl aurine, resorcinebenzeine, &c. Even the eosines have been to a very great extent superseded by azo-dyes.

With a note on p. 41 we are quite unable to agree. Says the author—"The custom of mixing colouring-matters for sale with indifferent substances, such as sodium sulphate or chloride, magnesium sulphate or dextrine, is not to be regarded as sophistication." Now the dyer and the tissue printer are not practically inconvenienced by the presence of a small percentage of dextrine. But supposing colours so treated are used for the manufacture of so-called aniline inks. The great advantage of such inks is that they contain no gummy matter, and therefore dry instantly and leave no deposit on the pen. But if dextrine is present this advantage is sacrificed.

In the tenth chapter the author describes certain bodies which are certainly obtained from coal-tar, but which have no tinctorial properties, such as kairine, thalline, antipyrine, and saccharine.

Concerning the last-mentioned product he emphasizes the fact that it is not a food, and can therefore scarcely be thought of as a substitute for sugar. We find no reference to Prof. Ira Remsen's claim to the discovery of this compound.

The absolutely innocuous character ascribed to salicylic acid may very safely be called in question.

In the last chapter figure murexide (now merely of historical interest), galloflavine (which has a doubtful future on account of its want of permanence to light), the "patent colours" of Croissant and Bretonnière (known in France as "cachou de Laval"), and canarine (which is very fast, but not beautiful).

This work demands our almost unqualified approval, and may be warmly recommended to all tinctorialists who can read German.

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*A New Basis for Chemistry: a Chemical Philosophy.* By Thomas Sterry Hunt, M.A., LL.D. (Cantab.). Boston: Cassino. London: Trübner and Co.

This work, though it deserves and will well repay a most careful study, is liable to be viewed in many quarters as heretical. The author repudiates the introduction of the atomic hypothesis into chemistry, though fully admitting definite combination by weight and by volume. He views chemical union as "an identification not only of the volumes (interpenetration mechanically considered), but of the specific characters of the combining bodies, which are lost in those of the new species." He says again:—"Nature builds up her units by interpenetration and identification, and not by juxtaposition of the chemical elements."

With Oken, whose influence we recognise throughout his teachings, he accepts the production of the chemical

elements from a primal undifferentiated matter, "Urstoff" or "protyle."

He complains of the tendency of modern students, who confound dynamical activities with chemism itself, thus losing sight of the essential nature of the chemical process. As examples of this confusion he brings forward utterances of Clifford, Faraday, and Helmholtz. Faraday expressed his "conviction that the forces termed chemical affinity and electricity are one and the same." Helmholtz is quoted as saying—"I think the facts leave no doubt that the very mightiest among the chemical forces are of electrical origin, . . . . but I do not suppose that other molecular forces are excluded, working directly from atom to atom."

The atomic hypothesis is examined at some length in the eighth chapter. Dr. Hunt refers to Whewell's "History of the Inductive Sciences" (vol. i., Book vi., chap. 5). This writer declares that "the atomic doctrines, when they are tried upon the general range of chemical observation, prove incapable of even expressing, without self-contradiction, the laws of phenomena." Chemical facts not only do not prove the atomic theory as a physical truth, but they are not, according to any modification yet devised by the theory, reconcilable with the scheme." Further:—"When we would assert this theory, not as a convenient hypothesis for the expression or calculation of the laws of nature, but as a philosophical truth respecting the constitution of the universe, we find ourselves checked by difficulties of reasoning which we cannot overcome, as well as by conflicting phenomena which we cannot reconcile.

Dr. Hunt himself says, quoting—as he does largely in the present treatise—one of his own earlier works, if "the volumes of the uniting species are always merged in that of the new one, . . . the atomic theory, as applied by Dalton, which makes combination consist in juxtaposition, is untenable." It is, further, unnecessary for explaining the law of definite proportions. "If the law of volumes is universal, and if the production of liquids and solids by the condensation of vapours is a process of chemical union or integration, giving rise to polymeres, the equivalent weights of which are as much more elevated as their densities are greater than those of the vapours which combine to form them, the application of the hypothesis of atoms and molecules to explain the law of definite proportions and the chemical process is not only unnecessary but misleading." For a further development of this argument the reader may turn to a paper on "The Law of Volumes in Chemistry," given in the Chemical News (vol. liv., p. 206).

The transference of the atomic hypothesis from the theory of dynamics to the theory of chemistry, the author considers as springing from that confusion between dynamical and chemical actions to which he has already referred. Elasticity, the movements of gases and liquids, the phenomena of temperature, electricity, and radiant energy, seem to most physicists most intelligible if we assume that the species which is the seat of the phenomena has a structure not continuous but made up of discrete molecules or atoms of a definite and constant size, which in liquids and solids varies for each species. But, however this may be, Dr. Hunt argues that its acceptance or rejection has no direct bearing on chemism, which considers the species not as such, but merely with reference to the species from which it has been derived, or into which it may pass by processes of integration or disintegration.

On a former occasion he raises the question—"Are we not going beyond the limits of a sound philosophy when we endeavour by hypotheses of hard particles with void spaces, of atoms and molecules with bonds and links, to explain chemical affinities, and when we give a concrete form to our mechanical conceptions of the great laws of definite and multiple proportions to which space is subordinated? It must not be inferred, as might be easily done, that Dr. T. S. Hunt repudiates the use of rational and structural formulæ. If like Gerhardt and many others who have used such formulæ most successfully we remember that they are not intended to represent the actual position of atoms or the shape of molecules, but to make evident, in the simplest and most direct manner, the relations which connect bodies with one another, in their transformations they have, the author considers, "an important place in chemical teaching."

The salient points of Dr. Hunt's views are the rejection—or rather the non-acceptance—of the atomic theory; the representation of chemical union as not juxtaposition but identification; the distinction between chemical and dynamical action, and the relegation to the latter sphere of the phenomena of radiant energy, temperature, and electricity manifested in chemical changes. Liquid and solid species may be represented as polymers of some primary species. The generation of species dissimilar to the parents, by heterogeneous change, such as the union of hydrogen and carbon to form acetylene, he terms metagenesis. On the other hand, the generation of species like the parents in percentage composition, by homogeneous change, he calls metamorphosis. Steam, he considers, passes by polymerisation into the two distinct species, water and ice.

We will, however, make no further extracts, hoping that some of our readers will make themselves acquainted with this volume and find in it suggestions for research.

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*Chemistry for Beginners:* adapted for the Elementary Stage of the Science and Art Departments' Examinations in Inorganic Chemistry. By R. L. Taylor, F.C.S., F.I.C., Teacher of Chemistry and Physics in the Central Higher Grade Board-School, Manchester. London: Sampson Low, Marston, Searle, and Rivington.

The shower of elementary treatises on chemistry which has prevailed for some years shows signs of abating, and will, we hope, cease until some capital discovery renders it necessary to revise the foundations of the Science. Like many—in our opinion, at least, too many—of its predecessors, this book is distinctly and avowedly examinational in its aims. It teaches such portions of chemistry and in such a manner as are required to enable the student to "pass" a certain examination. If we grant that this is the legitimate object in science-teaching—and in England it is almost forced alike upon teacher and pupil—we must admit that Mr. Taylor has accomplished his task in a very creditable manner.

At the end of the book we find the usual array of questions, though we are not informed whether they have been actually asked by the "Department" on former occasions.

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# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 21, May 23, 1887.

General Law of the Vapour-Tension of Solvents.—F. M. Raoult.—One mol. of a fixed non-saline substance, whilst dissolving in 100 mol. of any volatile liquid, reduces the vapour-tension of such liquid by an almost constant fraction of its value, bordering upon 0·0105.

On Double Copper and Ammonium Iodides.—André Saglier.—The author has obtained a series of these compounds by causing copper hydroxide to react upon a

solution of ammonium iodide, with or without an excess of iodine.

**Action of Heat upon Clays.**—H. Le Chatelier.—The author remarks that hydrated aluminium silicates, in spite of their common occurrence and their important industrial uses, are little known as regards their chemical constitution. They form, generally, mixtures so complex, that analysis alone furnishes no precise data as to their nature. He considers that by studying the temperature of dehydration of these bodies it may be possible to identify a small number of chemical species, and to distinguish the presence of each of them in different mixtures. If a small quantity of clay is rapidly heated, there takes place, at the moment of dehydration, a retardation in the rise of temperature, and this point may be utilised for establishing a distinction between the various hydrated aluminium silicates. In some cases there occur, also, sudden accelerations, indicating reactions attended by a liberation of heat. The clays examined may be referred to five very distinct types.

**On Erythrene Bromides.**—E. Grimaux and Ch. Cloëz.—An account of the tetrabromide and the dibromide.

**On Cyanacetophenone.**— Alb. Haller.— This compound is obtained in the form of white needles, soluble in boiling water, alcohol, and ether, and very sparingly soluble in cold water and petroleum ether. Its melting-point (corrected) is 80·5°. The constitution of this ketone, which comprises a methylene group between two electro-negative groups, and its reaction with vegetable colours point to an acid function less decided than that of cyano-malonic and acetylcyanacetic ethers.

**Aniline Sebate and Diphenyl-sebacamide.**—Gustave Gehring.—If two mols. aniline are allowed to react upon one mol. sebacic acid dissolved in alcohol, the aniline behaves like an ammonia, combining entirely with the acid without elimination of water. By evaporation in a vacuum, aniline sebate is obtained in transparent rhomboidal laminæ, colourless, and of a silvery lustre. It melts at 134°, and sublimes unchanged. Diphenyl-sebamide is obtained by heating in a flask, fitted with a refrigerating tube, equal weights of sebacic acid and aniline. The mixture melts at 110°, and boils at 180°. It is heated for sixteen hours, the temperature being raised at the end to 215°. The product is pulverised and re-crystallised several times from boiling alcohol. The compound is neutral to reagents, forms small colourless, nacreous, rhombic scales, tasteless and inodorous. It melts at 198°, and sublimes, unchanged, at 360°.

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*Journal de Pharmacie et de Chimie.*
Series v., Vol. xv., No 7, April 1, 1887.

**Incompatibility of Nitrates and Superphosphates.**—A. Andouard.—Already noticed under *Comptes Rendus*.

**Assay of Quinine Sulphate by Means of Neutral Potassium Chromate.**—J. E. de Vrij.—The reagent is a solution of 5 grms. neutral potassium chromate, very pure, in 100 c.c. distilled water, so that each c.c. contains 5 centigrms. of the salt. Two grms. of quinine sulphate are dissolved in 80 c.c. of boiling water, and 10 c.c. of the chromate solution are added. After the mixture has been kept for two hours at a temperature not exceeding 15°, stirring from time to time with a rod, it is thrown upon a filter. The crystalline quinine chromate remains upon the filter, whilst the filtrate contains merely a trace of dissolved quinine sulphate, 0·0378 part in 100 parts of the liquid if the sulphate is pure. In this case the liquid is not rendered turbid by the addition of a few drops of caustic soda. It remains clear after having been rendered alkaline, boiled, and allowed to cool again. If the sulphate contains cinchonidine, or others of the cinchona alkaloids, these bases are separated out under the same conditions. If the sulphate in question contains only one per cent cinchonidine sulphate, the filtrate rendered alkaline with soda remains limpid, even if heated to boiling. After cooling there is deposited at the bottom of the vessel a precipitate which is slight, but visible to the naked eye. If the quantity of foreign bases exceeds one per cent, the filtrate becomes turbid immediately after the addition of caustic soda, or at least after boiling.

**Reactions of Kairine, Antipyrine, and Antifebrine.**—C. A. Kohn.—In a dilute aqueous solution of kairine, a drop of ferric chloride gives, immediately, a violet colour, which quickly changes to a brown. An excess of ferric chloride in a strong solution of kairine gives a black-brown precipitate. Potassium dichromate gives, in a neutral solution of kairine an intense colouration, and a violet precipitate is shortly deposited. Antipyrine gives a red colour with ferric chloride, even in very dilute solutions; with nitrous acid a greenish blue colour is produced. Antifebrine gives no reactions with the above-named reagents.

**Assay of Potassium Iodide.**—M. Nicot.—The author prepares an acidified solution of sodium iodate, containing containing 4·78 grms. iodate, 15 grms. sulphuric acid, and distilled water enough to make up 1000 c.c. Fifty c.c. of this normal solution precipitate all the iodine contained in 100 c.c. of a pure 1 per cent solution of potassium iodide. One grm. of the sample is dissolved in 106 c.c. of distilled water, and the normal sodium iodate solution is added drop by drop from a graduated burette until a drop no lodger produces any colouration in the solution of iodide.

**Determination of Morphine.**— M. Dieterich.— The opium is treated with ten times its weight of water; to 50 grms. of the liquid extract are added 2 c.c. of normal ammonia (170 of caustic ammonia per litre) so as exactly to neutralise the liquid. The precipitate of narcotine is received upon a filter, and to 44·2 grms. of the liquid (=4 grms. of the opium) are added 10 grms. of ether and 4 c.c. of normal ammonia. The mixture is then set aside, stirring gently from time to time. After six hours the stratum of ether is drawn off, the mixture is again treated with 10 grms. of ether, the crystals of morphine are received upon a filter of 8 c.m. in diameter; they are twice washed with 5 c.c. of water, saturated with ether, dried at 100°, and weighed. All violent agitation of the extracting mixture and the ether must be avoided.

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*Bulletin de la Société Chimique de Paris.*
Vol. xlvii., No. 6, March 20, 1887.

**On Zinc Ferrite. Artificial Production of Franklinite.**—Al. Gorgen.—The author has succeeded in obtaining a zinc ferrite identical in composition with the natural product.

**Dissociation of Copper Sulphate.— Reply to an Observation by W. Müller Erzbach.**—H. Lescœur.—The author contends that the value of the dissociation-tensions cannot be deduced from Müller-Erzbach's determinations.

**Influence of Pressure and Temperature in the Action of Potassium Chloride upon Crude Carbonated Methylamine.**—J. A. Müller.—For the complete transformation of potassium chloride into bicarbonate, making use of 2·14 mols. of crude methylamine carbonate for a double mol. of potassium chloride, and employing carbonic acid diluted to 25 per cent, we may either effect the carbonation at the ordinary pressure, and at a temperature bordering upon 0°, or at the ordinary temperature and a pressure of about three atmospheres.

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*Bulletin de l'Association of the Pupils of M. Fremy.*
January, 1887.

**Artificial Production of the Ruby.**— M. Fremy.— This paper has already appeared in the *Compes Rendus*.

**Action of Fluorides upon Alumina.**—MM. Fremy and Verneuil.—Already noticed.

**Report on the Researches of M. Colson.**—M. Fremy.—The compound obtained by Wœhler on heating silicon in a lined crucible and considered by him as a silicon, is found to be a ternary compound, represented by the formula $Si_2C_2N$. In this body the carbon does not exist in a state of mixture, but of true combination, being, however, masked to such an extent that it does not burn if heated to redness in a current of oxygen. The same compound may be obtained by passing cyanogen over silicon at a red heat. M. Colson concluded that if this compound is formed by the union of nitrogen with the radicle $Si_2C_2$, this same silicon must be capable of uniting with other simple bodies, and he has, in fact, combined it with oxygen and with sulphur, obtaining the compounds $Si_2C_2O$, $SiCO_3$, and $Si_4C_4S$.

**Causes Determining the Phosphorescence of Calcium Sulphide.**—A. Verneuil.—Already noticed in the *Comptes Rendus*.

**Practical Analysis of Coal-Gas.**— M. Chevalet.—The author gives methods for the determination of hydrogen sulphide, carbon dioxide, oxygen, and carbon monoxide.

**Alloy-resisting Acids.**—M. Rettz has invented an alloy which offers great resistance to the action of acids and alkalies. It has the following composition :—

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**Chemical Examination of Commercial Glycerin.**—MM. Sulman and Berry determine the ash, the chlorides (volumetrically), the alkalinity, using litmus as indicator. The glycerins from stearine works contain from 0·5 to 2 per cent of alkalies, and the foreign organic matters.

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*Revue Universelle des Mines, de la Metallurgie, &c.*, Vol. xxi., No. 1, January and February, 1887.

**Aluminium and its Alloys.**—R. Van Langhenove.—The author describes the principal alloys of aluminium which he recommends for cannon and for the barrels of revolvers, as being cheaper than steel, lighter, and more resisting (7000 kilos. per square centimetre as against 4900 kilos.) ; aluminium silver, composed of aluminium, copper, and nickel; aluminium brass (5·8 Al, 26·8 Zn, and 67·4 Cu), and aluminium iron, containing 2 per cent of the former metal.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

**Regeneration of Nitric Acid.**—An apparatus for the continuous regeneration of nitric acid from the lower oxides of nitrogen on a large scale can be obtained from Mr. Ludwig Rohrmann, Krauschwitz near Muskau, Germany (Lunge and Rohrmann's Patent).—G. L.

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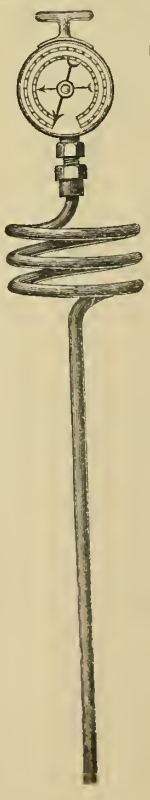

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THE CHEMICAL NEWS.

Vol. LV. No. 1440.

## HER MAJESTY'S JUBILEE.—A SCIENTIFIC RETROSPECT.

### III.

The progress of the chemical arts and industries has been no less striking than that of chemical theory and of analysis. Indeed it has attracted the notice of the outside public to a much greater extent.

The first event which we have here to notice is the removal of the last of the excise-burdens upon the chemical arts. Everyone must know that in the early part of this century the manufactures of printed tissues, of leather, glass, paper, starch, and soap, were subject to taxes, and that, to ensure the due collection of these imposts, the works were placed under constant Excise supervision, and were subject to regulations which rendered improvement nearly impossible. Though certain of these duties had been repealed before the accession of Her Majesty, yet the excise on glass was only removed in 1845, and that on soap in 1853.

We cannot here enlarge on a system which seemed to have for its object the repression rather than the encouragement of native industry. But we must not forget that, even beyond the boundaries of the "excised" industries, the progress of the chemical arts was rendered difficult and perilous. The revenue official might and did claim the power to enter and inspect (or at least it was not prudent to refuse him) any newly established manufactory, in order to satisfy himself that no contraband business was being there carried on. It is even recorded that the inventor of "British gum" was actually thrown into prison, although the starch which served as his raw material had been bought from a licensed manufacturer after full payment of duty. He was released, it is said, only through the influence of the elder Peel, the father of the great statesman.

A leading feature of the Victorian epoch has been the utilisation of waste materials and by-products. Any industry having such foundations occupies a somewhat precarious position. Some novel improvement may put an end to the output of the by-product or the waste in question. Thus the waste carbon from the manufacture of prussiate of potash was found capable of certain utilisations. But the production of prussiate is now so very limited that the supply of this carbon is practically at an end, and those who required it must look elsewhere.

A very successful use of waste matter has been, and still is, the recovery of soap and grease from the waste waters of fullers and woollen manufacturers. This waste is still produced, and its supply is not likely to fall short. But there are a number of processes, all depending upon cheap hydrochloric acid, and all placed in jeopardy by the decline of the Leblanc alkali process.

The condensation of the volatile matter given off in coke-burning has attracted no little attention, and has been to a certain extent successful. But the present low prices of sulphate of ammonia and of tar-products render the profits of this recovery comparatively trifling. Still the most important of all the utilisations of waste matter have been the artificial colours manufactured from coal-tar.

Not a few kinds of waste materials still await a profitable utilisation, such as the (ordinary) slag from blast-furnaces, the tank waste from the Leblanc alkali process, and the washings from dye-works, which often contain much colouring-matter.

Among the most important practical inventions made during the half century must rank the Bessemer process and the Thomas and Gilchrist method for dephosphorising iron ores. Though both these capital improvements are of British origin they have proved of no especial benefit to British industry, since they have been at once adopted abroad. The basic slags from the Thomas and Gilchrist process are indeed, to a certain extent, displacing superphosphate. The manufacture of this latter substance, and of chemical manures in general, has had its rise, culmination, and, it must be added, its decline, within the Victorian era. Foreign competition renders the exportation of these products little remunerative, whilst the depression of agriculture during the last ten years has greatly curtailed the home market.

The alkali manufacture, though it originated in the last century, reached its climax between the years 1850 and 1870. Since that date it has been declining, especially in the Tyne district, and subsequently also in Lancashire. The causes are not far to seek: foreign competition, heavy import duties on British-made alkali and its by-products, and last, but not least, the rise of the ammonia-soda process. This invention, though of British origin, has been perfected in Belgium, and is, from a variety of reasons, more flourishing on the Continent than at home.

The manufacture of the coal-tar colours, though originating in England, flourishes much more in Germany, and even in Switzerland if we duly consider the unfavourable circumstances of the latter country, than with us. It is strange to look back now at the prophecies which were uttered when the manufacture of mauve, magenta, &c., first sprang up. Rarely have sanguine and admittedly plausible expectations been more signally falsified. If we make every allowance for the skill of the German chemists, who are trained not to pass examinations but to conduct researches, we must admit that a great part of the blame rests with our laws, which permit goods made in infringement of British patents to be sent to this country from abroad, provided that they are forwarded directly to the consumer and not sold here through agents, and which, on the other hand, allow aliens to hold and uphold a British patent without ever working it on British soil or granting licenses for such working.

The ultramarine manufacture, conducted so successfully in Germany and in France, does not seem to take root in this country. Ultramarine of excellent quality is indeed made in Britain, but on a limited scale, and we still derive the bulk of our supply from abroad.

Extracts of dye-woods, so extensively used by our dyers and printers, seem to be less extensively manufactured at home than formerly. French and American makes are preferred by many consumers.

One of the most important inventions of the epoch has been the production of paraffin wax and oil from the oil-shales of Scotland. This trade seems at present in a depressed state, due to the competition of American and Russian mineral oils.

The utilisation of sea-weed on the western coasts of Scotland and Ireland has its ebbs and flows. Iodine and bromine are now more abundantly obtained from other sources; but Mr. Stanford's discovery of algine has, we believe, a great future before it, though, like many other valuable novelties, it is slow in coming into general use.

In tissue-printing we seem still to keep ahead of the world as far as quantity is concerned, though the best designs are produced in Paris and the finest work is turned out in Alsace.

A serious reflection is that in spite of all the money we spend on technical and scientific education, and of all the self-laudatory speeches in which we indulge, the number of foreigners employed in the management of our industrial establishments seems not to decrease. One of two things must therefore be admitted: either we are naturally inferior to our Continental neighbours in aptitude for discovery and invention,—a conclusion which we shall be slow to accept in view of the men whom we have pro-

duced.—or our method of training is fundamentally wrong. Does the Science and Art Department ever seriously meditate on this alternative?

## NOTE ON THE ELECTRO-DEPOSITION OF ALLOYS, AND ON THE ELECTROMOTIVE FORCES OF METALS IN CYANIDE SOLUTIONS.*

By SILVANUS P. THOMPSON, D.Sc., B.A.

It is known that the electro-deposition of such alloys as brass, bronze, and German silver is not practicable from mixed solutions of the sulphates or chlorides of the constituent metals, but can be accomplished by using cyanide solutions or neutral solutions containing cyanide of potassium in excess, thereby apparently departing from the law of Berzelius, that out of a solution of mixed metals the least electro-positive metal is deposited first.

To ascertain the cause of these facts the author has investigated—

(*a.*) The electromotive forces of a number of metals in aqueous solution of cyanide of potassium.

(*b.*) The dependence of these electromotive forces, in particular those of copper and zinc, upon the degree of concentration of the solution.

(*c.*) The variation of the electromotive forces of copper and zinc in a standard solution of cyanide of potassium at varying temperatures.

(*d.*) The electromotive forces of zinc and copper in a "brassing" solution consisting of the mixed cyanides of zinc and copper, having excess of cyanide of potassium present, and their variation at different temperatures.

It is found that the effect of higher concentration of the cyanide solutions is invariably to increase the electromotive force of copper more than it increases that of zinc.

In a cold dilute solution of cyanide of potassium the electromotive force of zinc against carbon is 1·158 volts, while that of copper against carbon is 0·948 volt, or zinc is 0·210 volt higher than copper. In a boiling saturated solution of cyanide of potassium, the electromotive force of zinc against carbon is 0·768 volt, and that of copper against carbon is 1·300 volt; or copper is 0·532 volt higher than zinc.

It is therefore possible to construct a voltaic battery containing one metal only, namely copper, and one electrolyte only, namely an aqueous solution of cyanide of potassium, kept hot at the anode and cold at the cathode of the cell.

In cyanide solutions containing about the following number of grms. of cyanide to the litre, the following were the electromotive forces observed with a carbon cathode:—

| Solution containing per litre | | | | | |
|---|---|---|---|---|---|
| 99·4 grms. | | 191·4 grms. | | 1·18 grms. | |
| Metals at 18° C. | | | | | |
| Zinc .. | 1·520 | Copper .. | 1·434 | Zinc .. | 1·13 |
| Copper .. | 1·425 | Zinc .. | 1·401 | Brass .. | 0·58 |
| Brass .. | 1·400 | Brass .. | 1·315 | German silver | 0·50 |
| German silver | 1·05 | German silver | 0·936 | Lead .. | 0·44 |
| Gold .. | 0·885 | Gold .. | 0·834 | Copper .. | 0·39 |
| Silver .. | 0·845 | Silver .. | 0·810 | Silver .. | 0·39 |
| Lead .. | 0·64 | Lead .. | 0·609 | Gold .. | 0·34 |
| Iron .. | 0·47 | Iron .. | 0·181 | Steel .. | 0·30 |
| Steel .. | 0·44 | Steel .. | 0·161 | Iron .. | 0·30 |
| Platinum | 0·27 | Platinum | 0·017 | Platinum | 0·14 |
| Carbon .. | 0 | Carbon .. | 0 | Carbon .. | 0 |

* A Paper read before the Royal Society, June 16, 1887.

Several of the metals exhibit maximum electromotive force at an intermediate concentration.

The following figures were obtained for zinc and copper in solutions of cyanide of varying strengths at 17° C.:—

| Grms. per litre. | E.M.F. zinc. | E.M.F. copper. | Difference Z—C. |
|---|---|---|---|
| 2·9 .. .. | 1·158 | 0·948 | +0·210 |
| 5·9 .. .. | 1·167 | 0·967 | +0·200 |
| 11·2 .. .. | 1·184 | 1·018 | +0·166 |
| 23·8 .. . | 1·221 | 1·058 | +0·163 |
| 47 7 .. .. | 1·269 | 1·130 | +0·139 |
| 95·5 .. .. | 1·303 | 1·220 | +0·080 |
| 191·1 .. .. | 1·355 | 1·360 | −0·005 |

In a mixed solution of cyanides of zinc and copper there is a neutral condition where the electromotive forces of zinc and copper are equal, and this neutral condition varies with the relative amounts of metal present, with the concentration of the solution, and with the temperature. The neutral temperature for a solution of given concentration is lowered by adding cyanide of potassium, and is raised by adding ammonia. The neutral point, however, is not well defined, the behaviour of copper being very uncertain; in general the electromotive force of clean copper in a cyanide solution rises, in some cases, as much as 0·06 volt, in a few seconds after immersion, but is rapidly though temporarily lowered on agitation.

Since the degree of concentration of the solution greatly affects the electromotive force of the metal, and since, in the act of deposition of a metal from its solution, the concentration of the liquid around the cathode is reduced, owing to slowness of diffusion, it follows that in electro-deposition the counter electromotive force at the cathode will vary with the rate at which metal is being deposited, and will, therefore, vary with the current-density employed. And since, moreover, the variations in electromotive force due to differences of concentration are greater for copper than for zinc, it follows that in the deposition of brass from a mixed solution of cyanides of a medium concentration, in which zinc is slightly more electro-positive than copper, there will be a certain density of current with which the metals will be deposited in nearly equal quantities, while for weaker current densities the less electro-positive metal will be deposited in excess, and for stronger current-densities the more electro-positive metal will be deposited in excess.

Hence, to variations in the concentration of the electrolyte near the cathode are due the departures, observed with all currents except weak ones, from the law that out of a solution of mixed metals the least electro-positive is deposited first.

## DISPERSION EQUIVALENTS.*

By J. H. GLADSTONE, Ph.D., F.R.S.

### Part I.

The idea of refraction equivalents has become familiar to those who work on the borderland of optics and chemistry, and the value of that property as a means of investigating the chemical structure of compounds is becoming more and more recognised. There is a similar property, perhaps equally valuable for the same object, which has attracted little attention hitherto; I allude to the equivalent of dispersion. During the last twelve months, however, I have collated old measurements of the length of the spectrum, whether made by myself or by others, and have added many new determinations, and I am now in a position to submit some of the results to the Society.

The history of the subject goes back to the first paper

* A Paper read before h R ne 16, 1887.

of Mr. Dale and myself upon the refraction of light,* in which we gave as one of the conclusions "the length of the spectrum varies as the temperature increases." In our second paper† we came to the conclusion that "there is no simple relation holding good for different liquids between the increase of volume and the decrease of dispersion by heat," contrary to what we found to be the case with refraction. We adopted $\mu_H - \mu_A$, *i.e.*, the difference between the refractive indices for the solar lines A and H as the measure of dispersion. This, divided by the density, gave the specific diversion. When, however, Landolt adopted the plan of calculating the "refraction equivalent," we applied the same method to what we termed the dispersion equivalent, that is, "the difference between $P\frac{\mu_A - 1}{d}$ and $P\frac{\mu_H - 1}{d}$, or more simply $P\frac{\mu_H - \mu_A}{d}$," where $d$ equals the density of the substance and P its atomic weight.

In two communications made to the British Association,‡ we stated that the dispersion equivalent of any substance is little affected by the manner in which it is combined with other bodies, and we gave as the mean value of $CH_2$ 0·35 in the vinic group, but higher figures in the benzene and pyridine groups; phosphorus equal to 2·9; chlorine 0·5; bromine 1·3; and iodine 2·6. In my subsequent paper in the *Philosophical Transactions*,§ in which the refraction equivalents of forty-six elements were worked out, I remarked, "the question of dispersion equivalents is also of interest; the data for the investigation of the matter are given in the Appendix." But there the matter rested. The paramount interest of the refraction equivalents in truth caused both the Continental observers and myself to neglect the question of dispersion; and with the exception of brief references to it in papers on Refraction,‖ nothing was published on the subject till last summer, when I applied the measurement of dispersion to the elucidation of the chemical structure of the essential oils;¶ and afterwards in a paper at Geneva** I ventured to give approximate values for fifteen elements.

Almost simultaneously with these appeared a paper by Brühl,†† in which he endeavoured to eliminate the influence of dispersion from the refraction equivalents of highly refractive bodies. In this he seems to establish the fact that, for such bodies at least, the theoretical formula of Lorenz $\frac{\mu^2 - 1}{(\mu^2 + 2)d}$, gives more uniform results than the empirical formula $\frac{\mu - 1}{d}$; but he draws as one of his conclusions, "the dispersion exercised by different bodies stands in no relation which is as yet clearly recognisable and measurable either with the refraction exerted by them, or with the chemical nature of the substances." In this and a following paper‡‡ he gives additional proof of the worthlessness of Cauchy's dispersion formula, or any of the suggested modifications of it, to eliminate the influence of dispersion.

It will be seen that Brühl's conclusion is inconsistent with the views I have recently expressed, and the determinations I had already published; but while I am free to confess that there are many difficulties in the investigation of dispersion which have not been felt in dealing with refraction, I hold that the following conclusions are fully warranted by the data:—

1st. That dispersion, like refraction, is primarily a question of the atomic constitution of the body; the general rule being that the dispersion equivalent of a compound is the sum of the dispersion equivalents of its constituents.

2nd. That the dispersion of a compound, like its refraction, is modified by profound differences of constitution; such as changes of atomicity.

3rd. That the dispersion frequently reveals differences of constitution at present unrecognised by chemists, and not expressed by our formulæ.

In this paper my object will be to point out the uniformity that does exist, leaving apparent exceptions for future consideration.

Before entering upon an attempt to determine the dispersion equivalents of the different elementary substances, it may be well to consider the difficulty which occurred at the threshold of the enquiry: and another which appears to have deterred Brühl from prosecuting his enquiries in the direction of dispersion.

The original experiments of Mr. Dale and myself led to the belief that the "specific dispersion, $\frac{\mu_H - \mu_A}{d}$, slightly diminishes with increase of temperature;" but more accurate experiments made on the same specimens of bisulphide of carbon, benzene, brombenzene, and mint terpene, at the temperature of the observing room in the height of summer and depth of winter, have made me less confident of this conclusion. The variations are certainly within the limits of experimental error. The observations of Wüllner both upon bisulphide of carbon and water, those of Baille and v. d. Willigen upon water, as well as those of Pisati and Paternó on benzene and cymene, show that there is little, if any, appreciable difference in the specific dispersion at different temperatures. The general tendency of the observations on the seventy substances which have been examined more or less carefully, appears to be that the small difference of specific refraction that exists at different temperatures is a little greater in the case of H than in that of A.

Brühl gives three cases of isomeric or quasi-isomeric bodies. He measures the specific dispersion by the B of Cauchy's formula divided by the density. He shows that cinnamic alcohol, $C_9H_{10}O$, and cinnamic aldehyd, $C_9H_8O$, both of which he conceives to contain four pair of doubly-linked carbon-atoms, have a widely different specific dispersion; that allyl paracresolate and anethol, $C_{12}H_{12}O$, having four pair of doubly-linked carbon-atoms, are also quite different in dispersion; and that, on the other hand, cymol and hexahydronaphthalin, both having the formula $C_{10}H_{14}$, but the first three pair, and the second two pair of doubly-linked carbon-atoms, have nearly the same dispersion. But if we reckon out the refraction equivalents for cinnamic aldehyd and for anethol from the numbers given in the same table, it will be seen that they are inconsistent with the supposition that these bodies have the chemical structure that he attributes to them; in fact the extremely high dispersion in each case only tells the same tale as the extremely high refraction. As to the two substances of the formula $C_{10}H_{14}$, it is open to question whether hexahydronaphthalin has only two pair of doubly-linked carbon-atoms; and the refraction equivalent calculated for each of the specimens throws some doubt upon their purity. Brühl also compares methyldiphenylamine with cinnamic aldehyd, but the presence of nitrogen in the first body, and the uncertainty as to the constitution of the second, render it unsafe to draw any conclusions from the comparison. That the specific dispersion of isomeric or polymeric bodies is practically the same, except where the constitution is very different (as in aniline and picoline), was shown in my paper in the *Philosophical Magazine* six years ago; and this must be set against the doubtful cases mentioned above.

### *The Elements.*

There are but few of the elements of which the dispersive energy can be directly determined; but it so happens that

* "On the Influence of Temperature on the Refraction of Light," *Phil. Trans.*, 1858, p. 8.
† "On the Refraction, Dispersion, and Sensitiveness of Liquids." *Phil. Trans*, 1863, p. 323.
‡ *Brit. Assoc. Rep.*, 1886. (*Trans. Sec.*, pp. 10 and 37.)
§ "On the Refraction Equivalents of the Elements." *Phil. Trans.*, 1869, p. 27.
‖ *Phil. Mag.*, vol. xi., 1881, p. 59; *Brit. Assoc. Rep.*, 1881 (*Trans. Sec.*, p. 591). *Chem. Soc. Journ.*, vol. xlvi., 1884, p. 259.
¶ *Chem. Soc Journ.*, vol. l., 1886, p. 609.
** *Archives Sci. Phys. Nat.*, vol. xvi., 1886, p. 192.
†† *Liebig's Annalen*, vol. ccxxxv., 1886, p. 1.
‡‡ *Liebig's Annalen*, vol. ccxxxvi., 1886, p. 233

two or three of these are among the most dispersive of bodies.

*Phosphorus* was determined by Mr. Dale and myself in a melted condition, and also by Damien both in that and the solid state. Our observation gives 3·1; those of Damien* work out at 2·9 and 2·8 respectively.

*Sulphur.*—An old observation of mine on this body liquefied, gave 0·90 for E−A; and recent observations from its solutions in bisulphide of carbon give 1·2 for F−A. These agree in indicating about 2·6 for H−A.

*Selenium.*—According to the observations of Sirks,† the refractive indices for A and D are respectively 2·653 and 2·98; taking the specific gravity at 4·5, the dispersion equivalent of this element would be the extraordinary amount of 5·67 for D−A alone.

*Hydrogen.*—Ketteler's‡ observations give a dispersion equivalent of 0·0152 for the difference between the green line of thallium and the red line of lithium.

*Carbon.*—Schrauf's§ observations upon diamond give 0·058 for the dispersion equivalent of the same range.

*Iodine*, in the state of vapour, or dissolved in bisulphide of carbon, gives a spectrum in which the order of the colours is abnormal.

Far more important results have been obtained from organic substances, by following a method similar to that which Landolt adopted in his determination of the refraction equivalents of carbon, hydrogen, and oxygen. The materials for such an enquiry are very abundant. They consist of the observations published by Mr. Dale and myself in 1863, and my more recent determinations published and unpublished; the very valuable lists of Landolt and Brühl, numerous observations by Kanonnikoff, Nasini, and others. The Continental observers have usually adopted the lines $\alpha$, $\beta$, and $\gamma$ of the hydrogen spectrum.

On comparing the refraction equivalents of organic liquids of the fatty acid series which differ from one another by $CH_2$, or multiples of it, my best determinations lie between 0·33 and 0·36, averaging about 0·35 for each $CH_2$. On treating in a similar manner fifteen series of such bodies in Brühl's tables, some of which contain many terms, the dispersion equivalent for $\gamma-\alpha$ works out very uniformly at an average of 0·215. This answers to 0·342 for H−A. Armstrong's cymhydrene, which is a saturated substance of the formula $C_{10}H_{20}$, has a dispersion equivalent of 3·44, giving therefore 0·344 for each $CH_2$. Kanonnikoff's determinations of tetraterpene and naphthene, also $C_{10}H_{20}$, give similar numbers. It may therefore be assumed that the value of $CH_2$ in saturated organic compounds lies between 0·34 and 0·35, answering to the well known 7·6 as the refraction equivalent of the same combination. When, however, we examine unsaturated compounds in a similar manner, we find that the value rises to at least 0·40.

*Hydrogen.*—While the value of $CH_2$ may be fairly taken at 0·34, it is more difficult to say what portion of this is due to the carbon, and what to the hydrogen. I have endeavoured to determine it, by deducting $n$ times $CH_2$ from the paraffins $C_nH_{2n+2}$; by comparing the monatomic, diatomic, and triatomic alcohols, and by other similar means. The results are somewhat irregular, as might indeed be expected from the smallest of the residual figure, but give a mean of 0·04 per each hydrogen.

*Carbon.*—If the $H_2$ in $CH_2$ be taken at 0·08, it follows that the carbon will have a dispersion equivalent of about 0·26. This answers to the refraction equivalent of 5·0.

It is well known, especially from the researches of Brühl, that in unsaturated organic compounds there is an increase of refraction, for the line A, of about 2·2 for each pair of doubly-linked carbon-atoms. Assuming this to be due to a different value for carbon, we obtain a refraction equivalent of 5·0+1·1, *i.e.*, 6·1. In all such cases there is a great increase of dispersion; this increase, however, is not always the same. In the allyl compounds, whether determined by Brühl, Kanonnikoff, or myself, it is uniformly very close to 0·5. In the olefines it is the same. In the whole of the aromatic series it is at least 0·8. Coincident therefore with the higher refraction equivalent for carbon, we have two dispersion equivalents of about 0·26+0·25, and 0·26+0·40, *i.e.*, 0·51 and 0·66.

It must remain for future consideration whether there may not be an intermediate refraction equivalent, corresponding to the dispersion equivalent of 0·51.

On the appearance of Brühl's papers in 1880, I ventured to suggest that there was a still higher refraction equivalent for carbon, in those cases in which it "has all four of its units of atomicity satisfied by other carbon-atoms, each of which has the higher value of 6·0 or 6·1," as in naphthalene or pyrene. This view has been, and is, the subject of controversy, but on turning to the dispersion equivalents of these bodies, they are found to be always enormously high, far higher than can be accounted for by the figures with which we have hitherto been dealing.

*Oxygen.*—It has been established by Brühl, that in the case of aldehyds and ketones, oxygen has a refraction equivalent of 3·4. As these have the general formula $C_nH_{2n}O$, and the dispersion of $CH_2$ is known, it is very easy to determine the dispersion equivalent of the oxygen. Various determinations of these bodies give a fairly uniform result; viz., 0·18 for H−A.

In the case of the alcohols, the oxygen has a refraction equivalent of only 2·8. Comparing the dispersion equivalents of the alcohols of different atomicities in the published lists, the mean value for oxygen in this condition comes out at about 0·10. Nevertheless, in the organic acids and compound ethers, the value of the two oxygens together seems rarely if ever to exceed 0·24.

*Chlorine.*—Our lists also give us the means of determining the value of chlorine in organic substances of the fatty acid series. As reckoned from such substances as chloroform, chloral, ethylene, and ethylidine chloride, and bichloride of chlorethylene, the dispersion equivalent of this halogen appears to be 0·50, though in the simple chlorides of the compound radicles it appears to be a little less.

*Bromine.*—The dispersion equivalent of bromine varies in a similar way to that of chlorine. As deduced from bromoform and the dibromides of the olefines, it is 1·22; but in the bromide of ethyl it is lower.

*Iodine.*—The dispersion equivalent of iodine in di-iodide of methylene was found to be 3·65, and in iodoform in solution it seems to be about the same; while in the ordinary iodides of the compound radicles it is much less.

*Nitrogen.*—Nitrogen appears to have a lower value in nitriles, cyanides, and sulphocyanides than in organic bases: but the figures obtained so far, for each condition of nitrogen, are not accordant. The lower value, however, probably does not exceed 0·10. The values of $NO_2$ in the fatty acid series, as deduced from substitution products of the alcohols, glycerin, mannite, &c., are, however, fairly accordant, giving about 0·82.

*Sulphur.*—For the determination of sulphur, we have the excellent observations of Wiedemann,* and Nasini;† the first on sulphur substitution products of carbonic ethers, the second on many organic compounds. There exist also two or three observations of my own. It appears that the value of sulphur in mercaptans, sulphocyanides, and sulphides of ethyl, butyl, amyl, and allyl, is about 1·21; answering to the refraction equivalent of 14·0.

But in bisulphide of carbon, where the refraction equivalent of sulphur is 16·0, the dispersion equivalent is 2·61: and this is about the value which the element appears to have in the isosulphocyanides, while the element itself dissolved in bisulphide of carbon, gives 1·20 for the dispersion F−A, which is equivalent to fully 2·5.

* *Journal de Physique*, 1881.
† *Poggendorff, Annalen*, vol. cxliii., 1871, p. 429.
‡ *Poggendorff, Annalen*, vol. cxxiv., 1865, p. 390.
§ "Ueber das Dispersionsäquivalent von Diamant." *Wiedemann, Annalen*, vol. xxii., 1884, p. 424.

* *Journ. Prakt. Chem.*, vol. cxiv., 1873, p. 453.
† *Gazz. Chim. Ital.*, vol. xiii., p. 296.

These results are collected together in the following table. The dispersion equivalents here given, must, however, not be taken for anything more than approximate.

| Substance. | Atomic Weight. | Refraction Equivalent A. | Dispersion Equivalent H−A. |
|---|---|---|---|
| Phosphorus .. .. .. | 31 | 18·3 | 3·0 |
| Sulphur, double bond | 32 | 16·0 | 2·6 |
| ,, single bonds | ,, | 14·0 | 1·2 |
| Hydrogen .. .. .. | 1 | 1·3 | 0·04 |
| Carbon .. .. .. .. | 12 | 5·0 | 0·26 |
| ,, .. .. .. .. | ,, | 6·1 ? | 0·51 |
| ,, .. .. .. .. | ,, | 6·1 | 0·66 |
| Oxygen, double bond .. | 16 | 3·4 | 0·18 |
| ,, single bonds .. | ,, | 2·8 | 0·10 |
| Chlorine.. .. .. .. | 35·5 | 9·9 | 0·50 |
| Bromine.. .. .. .. | 80 | 15·3 | 1·22 |
| Iodine .. .. .. .. | 127 | 24·5 | 3·65 |
| Nitrogen .. .. .. | 14 | 4·1 | 0·10 |
| $CH_2$ .. .. .. .. | 14 | 7·6 | 0·34 |
| $NO_2$ .. .. .. .. | 46 | 11·8 | 0·82 |

It will be seen by a glance at this table that the dispersion equivalents of the elementary substances are not in proportion to their atomic weights, or, in other words, that they have different specific dispersive energies. Thus the analogous elements, sulphur and oxygen, are strongly contrasted in this respect; their specific refractive energies being respectively 0·081 and 0·011. Again it will be evident that the proportion between the refraction and dispersion is not the same even in the case of analogous elements. Thus, taking the three halogens, the ratio between the refraction for A and the dispersion for H−A for chlorine is about 100 to 5, for bromine 100 to 8, and for iodine 100 to 15.

*Metals in Salts.*—In 1869, as already stated, I suggested that the same data from which the refraction equivalents of the metals had been determined would be available also for their dispersion equivalents. I have many observations in addition to the data then published; and Kanonnikoff has been over part of the same ground, measuring the $\alpha$ and $\beta$ of the hydrogen spectrum. Unfortunately, however, the errors of observation bear so considerable a proportion to the whole amount observed, at any rate in dilute solutions, that we cannot look upon single determinations of the dispersion equivalent of a salt as of much value. Thus, even when great care has been taken in measurement, each index of refraction is liable to an error of $\pm$0·0001, and as the error in determining A and H may be in opposite directions, $\mu_H - \mu_A$ cannot be relied upon within $\pm$0·0002. Now among solutions of salts the specific dispersion rarely amounts to 0·02; the error of observation may therefore be more than 1 per cent, and if the salt should form only 5 per cent of the solution, the error might exceed 20 per cent. Such solutions, therefore, are practically valueless for this purpose. Yet it would be easy to publish a table of miscellaneous salts, the dispersion equivalents of which had been deduced from several fairly accordant observations on fairly strong solutions, or which have been corroborated from some independent source. It has appeared preferable, however, to confine attention at present to the series of potassium and sodium salts, which are far the most complete and the most instructive.

It is evident at a glance that the figures in the sodium columns are invariably lower than those in the potassium columns, and that the difference is fairly uniform. In regard to the refraction equivalent, it is about 3·33,† and in the dispersion equivalent it is about 0·09.

It follows, that if we can determine the value of potassium, that of sodium may be at once calculated: and presumably the same process may be extended to all other metals that form soluble salts.

But it is not so easy to determine the value of potassium. In regard to the refraction equivalent, my original determination was 8·1; but Kanonnikoff gives only 7·75, which led me, three years ago, to recalculate the observations, taking Brühl's values for oxygen, and to reduce my previous estimate to 7·85. This is determined mainly from the organic salts, and the nitrate and cyanide. I did not draw any conclusion from the haloid salts, as the chlorine, bromine, and iodine in them appear to have somewhat higher values than what they have in organic compounds.

How are we to determine the corresponding equivalents of dispersion? From the haloid salts it would seem to be about 0·8, but it seems likely that the disturbing influence, whatever it be, which increases the refraction of the haloid salts, should affect the dispersion. The formate and acetate, $KCHO_2$ and $KC_2H_3O_2$, promise more trustworthy results, as we can subtract from their dispersion equivalents the numbers already determined for carbon, hydrogen, and oxygen. This will give respectively 0·53 and 0·44 for the dispersion equivalent of K.

If we view potassium hydrate, KHO, as water in which one hydrogen is replaced by potassium, water being 0·265, we obtain the value of 0·565 for K.

From the nitrite, $KNO_2$, by subtracting 0·82 for $NO_2$, we obtain 0·48 for K.

In like manner from the cyanide, KCN, by deducting 0·36 for cyanogen, we get 0·58 for K.

From the carbonate, $K_2CO_3$, by taking the probable value of the $CO_3$ at 0·60, we get 0·40 for each K.

From the oxalate, $K_2C_2O_4$, by deducting 1·00 we get 0·59 for each K.

These figures, varying from 0·40 to 0·59, are too uncertain, and too wide to give a good average. I doubt if such variations can be attributed wholly to experimental error; but, on the other hand, it is difficult to imagine that potassium should have more than one dispersion equivalent while in the same series of dissolved salts it has apparently one and the same refraction equivalent. I am more disposed to believe that the uncertainty lies in the value of radicles to which the metal is joined; but this will require a more extended research.

It is also an important enquiry:—To what extent does the modification of the dispersion equivalent affect the refraction equivalent for the line A? On this question, and others of a similar nature, I hope shortly to submit a further communication. I think it will be already

† Previously determined at 3·3.

| | Refraction Equivalent. | | | Dispersion Equivalent. | | |
|---|---|---|---|---|---|---|
| | Potassium. | Sodium. | Difference. | Potassium. | Sodium. | Difference. |
| Chloride .. .. .. .. .. | 18·83 | 15·40 | 3·43 | 1·27 | 1·18 | 0·09 |
| Bromide .. .. .. .. .. | 25·25 | 21·80 | 3·45 | 2·17 | 2·08 | 0·09 |
| Iodide .. .. .. .. .. | 35·78 | 32·52 | 3·26 | 4·42 | 4·33 | 0·09 |
| Hydrate .. .. .. .. .. | 12·60 | 9·26 | 3·34 | 0·79 | 0·72 | 0·07 |
| Formate .. .. .. .. .. | 20·01 | 16·60 | 3·41 | 1·07 | 0·96 | 0·11 |
| Acetate .. .. .. .. .. | 27·52 | 24·34 | 3·18 | 1·32 | 1·23 | 0·09 |
| Carbonate .. .. .. .. .. | 28·63 | 22·17 | 2(3·23) | 1·40 | 1·34 | 2(0·03) |
| Oxalate .. .. .. .. .. | 37·55 | — | — | 2·18 | | |
| Nitrite .. .. .. .. .. | 18·99 | 15·65 | 3·34 | 1·30* | 1·17 | 0 13 |
| Cyanide .. .. .. .. .. | 17·18 | — | — | 0·94 | | |

* This is estimated from measurements of A, F, and G, and is somewhat open to doubt, as there seems to be something abnormal in the spectrum

sufficiently obvious that the specific dispersive energy of a compound body is a physical property analogous to, but distinct from, its specific refractive energy; and that it is capable in like manner of throwing light upon chemical structure.

## ON KREATININS.*

I. On the Kreatinin of Urine, as distinguished from that obtained from Flesh-Kreatin.

II. On the Kreatinins derived from the Dehydration of Urinary Kreatin.

By G. STILLINGFLEET JOHNSON, M.R.C.S., F.C.S., F.I.C.

### Part I.

This investigation was suggested by a careful study of the reducing action of normal human urine upon picric acid in presence of potash at the boiling temperature.

The picric acid method for the quantitative estimation of sugar in urine was introduced by Dr. George Johnson in 1883. Whilst assisting him in working out the details of the process, the author's attention was drawn to the small amount of reduction exerted by *all* specimens of normal human urine. The average picric reduction observed was equal to that which would be effected by a solution of glucose containing 0·6 grain to 1 fluid ounce.

The reduction of cupric oxide in boiling alkaline solution was always somewhat greater, averaging 0·7 grain per 1 fluid ounce. Although many physiological chemists express the opinion that normal human urine contains always a little sugar, to which this reducing action is to be attributed, the author's researches have led him to an opposite conclusion.

The reducing agent of normal urine differs from glucose in producing some reduction of picric acid in presence of potassium hydrate at the ordinary temperature (*vide* Dr. R. Kirk, *Lancet*, June 16, 1883).

The reducing agent of normal urine cannot be made to undergo the alcoholic fermentation in presence of yeast. Nevertheless Dr. Pavy (*Med. Chir. Soc. Trans.*, vol. lxiii, p. 222) attributes one-fourth of the reducing action of normal urine upon cupric oxide to uric acid, and the remaining three-fourths to "the small amount of sugar naturally present in urine."

Brücke is also of opinion that normal human urine contains a small quantity of sugar.

Uric acid and kreatinin together are credited by Prof. E. Salkowski (*Centralblatt fur die Medicinischen Wissenschaften*, March, 1886) with from one-sixth to one-fifth of the total reducing action of normal urine, the remainder being due to "other substances, and very probably to compounds of glycuronic acid (*Glycuron-säure-verbindungen*)."

The author found that about three-fourths of the total reducing action of normal urine is destroyed by prolonged boiling with potassium hydrate, the remaining one-fourth being due to the survival of the uric acid, thus confirming Dr. Pavy's observation that one-fourth of the normal reducing action is due to uric acid.

On attempting to isolate the normal reducing agents by precipitants, it was found that mercuric chloride gradually effected complete precipitation of the reducing agent when added in sufficient excess to the unconcentrated urine. Complete precipitation can be effected in forty-eight hours if one-twentieth of its volume of a cold saturated solution of sodic acetate be first added to the fresh urine, then one-fourth of its volume of a cold saturated solution of mercuric chloride. The precipitate, which forms immediately, should be separated by filtration, as it contains no reducing agent except uric acid, which is probably present in it as mercuric urate; but the filtrate from the first amorphous precipitate begins to deposit the mercury salt of the reducing base in about half an hour. This deposit appears granular and crystalline, but under the microscope is found to consist of minute spherical masses. The weight of the dry spherical precipitate is always greater than that of the amorphous one weighed in the same condition. The desiccation must be conducted over sulphuric acid at the ordinary temperature, since the compound is decomposed at 100° C. in presence of water.

The filtrate from this granular (spherical) mercury salt is devoid of reducing action upon cupric oxide and picric acid. The spherical mercury salt of the reducing base (for the basic nature of the normal reducing agent is strongly indicated by the above results) is easily soluble in hydrochloric acid, but insoluble in acetic acid. Moistened with solution of potassium hydrate, the compound gradually blackens from reduction of mercury at the ordinary temperature, and much compound ammonia is evolved. Suspended in cold water and treated with hydrogen sulphide, the compound is decomposed, mercuric sulphide remaining undissolved, whilst the solution becomes acid in reaction and exhibits reducing properties On evaporating this acid solution a crystalline salt is obtained, which is the hydrochloride of the reducing base. As the spherical mercury salt, obtained as above from urine, appeared to be always quite homogeneous and pure, with the exception of a little colouring-matter, the exact weight of the compound obtained from known volumes of urine was next ascertained.

The samples of urine examined were in all cases ascertained to be free from albumen and sugar before precipitation. The filtrates from the first or amorphous precipitate, produced by mercuric chloride and sodic acetate, were allowed to collect in a large glass vessel, in which the spherical compound gradually accumulated. After standing some days the total precipitate was collected, washed with cold water, dried in a vacuum over $H_2SO_4$, and weighed.

(I.) 34,640 c.c. of urine gave 198 grms. of Hg salt, equivalent to 5·7 grms. of Hg salt per litre of urine.

(II.) 40,625 c.c. of urine gave 293·13 grms. of Hg salt, equivalent to 7·19 grms. of Hg salt per litre of urine.

The mean specific gravity in Experiment I. was 1·020, and the mean reduction of picric acid was equivalent to 0·67 grain glucose per 1 fluid ounce.

The mean specific gravity in Experiment II. was 1·022, and the mean reduction of picric acid was equivalent to 0·86 grain of glucose per 1 fluid ounce.

In my own case I found that the mean quantity of mercury salt obtained from the urine of twenty-four hours agreed very nearly with the above results, the total urine of six days having been carefully collected and examined each twenty-four hours.

The following table shows the weight of dry mercury salt of urinary kreatinin and of dry "1st mercury precipitate,"—*i. e.*, is the precipitate which is formed immediately when $HgCl_2$ is added to the fresh urine.

Weight of the body at the time of experiment, 70·08 kilogrammes.

| Date. | Vol. of Urine passed in 24 hours. | Weight of 1st Hg ppt. in grms. | Weight of 2nd Hg ppt. in grms. |
|---|---|---|---|
| Dec. 29—30 .. | 1790 c.c. | 5·355 | 9·076 |
| ,, 30—31 .. | 1360 ,, | 9·238 | 9·930 |
| ,, 31—Jan. 1 | 1575 ,, | 7·300 | 8·758 |
| Jan. 1—2 .. | 1230 ,, | 6·715 | 8·176 |
| ,, 2—3 .. | 1700 ,, | 4·985 | 8·932 |
| ,, 4—5 .. | 1275 ,, | 7·735 | 7·955 |

It will be seen from this table that the weight of the spherical mercury salt of the reducing kreatinin is always greater than that of the first or amorphous mercury precipitate, and that the weight of the former obtained from the total urine of twenty-four hours is much more constant than that of the latter.

* Abstract of a Paper read before the Royal Society, June 16, 1887.

From the above table the following averages are obtained :—

| | | |
|---|---|---|
| Average 1st Hg ppt. in 1000 c.c. .. .. .. | 4·62 grms. | Max. 6·8 Min. 2·93 |
| Average *spherical* Hg ppt. in 1000 c.c. .. | 5·9 ,, | Max. 7·3 Min. 5·07 |
| Average 1st Hg ppt. in 24 hours .. .. .. | 6·888 ,, | Max. 9·238 Min. 4·985 |
| Average 2nd Hg ppt. (spherical) in 24 hrs. | 8·804 ,, | Max. 9·930 Min. 7·995. |

Ratio of *kreatinin* excreted in twenty-four hours to body weight = 25 : 1,000,000.

The formula of the spherical mercury salt arrived at by analysis is $4(C_4H_7N_3O.HCl.HgO).3HgCl_2$.

It may here be observed that mercuric chloride has been recommended by Maly (*Ann. Chem. Pharm.*, vol. clix., p. 279) for preparing kreatinin from the urine of man or the horse. He does not mention the fractional precipitation by mercuric chloride, but recommends a preliminary concentration of the urine by heat, and precipitation by basic lead acetate before adding mercuric chloride. On repeating his process I found that even after the removal of the uric acid, &c., by basic lead acetate, the mercuric chloride still produced an immediate flocculent precipitate, followed by a granular one; and if the flocculent amorphous matter was not separated by filtration, the total mercury precipitate yielded a gummy mass after treatment with $H_2S$, which would not yield crystals until treated with alcohol, as Maly himself recommends. By my method, however, the hydrochloride of the reducing base is obtained in crystals after the first evaporation: these crystals contain chlorine in the proportion required by the formula $C_4H_7N_3O.HCl$.

The *platinum salt* of the reducing base is obtained in the form of anhydrous crystals, when an alcoholic solution of its hydrochloride is mixed with an alcoholic solution of platinic chloride. If these anhydrous crystals be dissolved in water, and the solution evaporated, or if the aqueous solution of the hydrochloride of the base be mixed with platinic chloride in aqueous solution and evaporated, fine orange-coloured prisms separate out, which have the formula $2(C_4H_7N_3O.HCl).PtCl_4.2H_2O$. Heated to 100° C. these crystals become anhydrous, yellow, and opaque.

The *free reducing base* is obtained from its hydrochloride by mixing the concentrated aqueous solution with excess of pure lead hydrate* *without heat*, and filtering; the alkaline filtrate by spontaneous evaporation deposits large square plates with bevelled edges, or long efflorescent prisms if great care is taken to avoid heating the solution of the hydrochloride. The aqueous solution of the free base is alkaline in reaction, intensely bitter to the taste, gives crystalline precipitates with zinc chloride, mercuric chloride, and picric acid, but none with silver nitrate, unless the solution be very concentrated.

The reducing base, which is undoubtedly the natural kreatinin of urine, when anhydrous, has the empirical formula $C_4H_7N_3O$, but the efflorescent kreatinin, obtained only when great care is taken to avoid heat, has the composition $C_4H_7N_3O.2H_2O$. After efflorescence this body has the same percentage composition as the anhydrous tabular kreatinin :—

One part by weight of the tabular kreatinin dissolves in 10·78 parts of water at 17° C.

One part of the tabular kreatinin dissolves in 362 parts of absolute alcohol at 17° C.

The efflorescent kreatinin (before efflorescence) dissolves in 10·6 parts of water at 14° C. The effloresced kreatinin requires 14 parts of water at 14° C. for solution.

The natural kreatinin of urine reduces cupric oxide in proportion as 12 : 10 parts by weight of glucose.

The average weight of this base passed by a healthy man in twenty-four hours (as determined by weighing the spherical mercury salt precipitated from the urine as above) is from 1·7 to 2·1 grms., equivalent in reducing action upon cupric oxide to from 1·5 to 1·75 grms. of glucose (= 23 to 27 grains of glucose in 52·8 fluid ounces of urine).

Therefore cupric oxide will be reduced by the normal urinary kreatinin in quantities equivalent to the reduction effected by 0·43 to 0·51 grain of glucose per 1 fluid ounce. The conclusion is that the total reduction effected by normal urine is accounted for by the uric acid and kreatinin which it contains.

There is every reason to believe that the natural kreatinin of urine is the efflorescent kreatinin,—

$$C_4H_7N_3O.2H_2O,$$

which is now described for the first time; for this compound is obtained only when the greatest care is taken to employ no *heat* throughout the process of extraction.

The following results of the re-crystallisation of this compound from aqueous solutions, made at different temperatures, indicate that the water ($2H_2O$) in this efflorescent base is not in the condition of simple water of crystallisation.

After efflorescence, if the effloresced kreatinin be dissolved in water at the ordinary temperature, the solution yields efflorescent kreatinin again on evaporation *in vacuo* over $H_2SO_4$.

But if the effloresced kreatinin be dissolved in water at 100° C., in quantity sufficient to hold the base in solution on cooling to the ordinary temperature, tabular anhydrous kreatinin is obtained when this solution is evaporated *in vacuo* over $H_2SO_4$.

Again, if the tabular kreatinin be kept in aqueous solution at 60° C. for some time, *efflorescent kreatinin* results when the cooled solution is evaporated *in vacuo* over $H_2SO_4$.

Further details on this point are to be found in the original paper.

### Part II.

The natural urinary kreatinin yields a kreatin when its dilute aqueous solution is subjected to prolonged ebullition; and this kreatin, when treated by Liebig's process, is converted into kreatinin hydrochloride.

This artificial kreatinin hydrochloride differs from the hydrochloride of the natural kreatinin of urine, in that it crystallises from cold aqueous solution in efflorescent crystals, whereas the hydrochloride of the natural base is always anhydrous.

Efflorescent and tabular kreatinins may be obtained from this hydrochloride, resembling in crystalline form and percentage composition those derived from the natural hydrochloride, but exhibiting some important differences. Thus the platinum salt of the artificial tabular kreatinin requires nearly twice as much water to dissolve it as that of the natural base at the same temperature.

Both the natural and artificial kreatinins form well-crystallised gold salts. The gold salt of the natural kreatinin is unchanged by ether, but that of the artificial base is decomposed thereby, the kreatinin hydrochloride separating out, and the auric chloride passing into solution.

Finally, the artificial kreatinins are less powerful reducing agents than the natural base.

Four mols. of the natural kreatinins are equivalent to two mols. of glucose.

Five mols. of the artificial kreatinins are equivalent to two mols. of glucose in reducing action.

Therefore artificial kreatinins must not be compared with the natural base as to their reducing action.

Prof. W. N. Hartley has observed a marked difference in the absorption spectra of the natural kreatinin of urine, and of an artificial kreatinin obtained by the author from flesh kreatin.

* The lead hydrate employed for removing chlorine from the kreatinin hydrochloride must be free from *basic nitrate*, otherwise lead will be found in the solution of the free base. The lead-hydrate which the author has found to give the best results is that obtained by precipitation of *lead acetate* by ammonia.

*Tabular Synopsis of Comparison between various Kreatinins.*

| | 1. Efflorescent kreatinin of urine, $C_4H_7N_3O.2H_2O$. | 2. Tabular kreatinin of urine, $C_4H_7N_3O$. | Efflorescent kreatinin from urinary kreatin, $C_4H_7N_3O.2H_2O$. | Tabular kreatinin $\alpha$ from urinary kreatin, $C_4H_7N_3O$. | 5. "Kreatinin" (Liebig). |
|---|---|---|---|---|---|
| Solubility of base in water .. .. .. | 1 in 10·6 parts at 14° C. | 1 in 10·78 parts at 17° C. | — | 1 in 10·68 parts at 16·5° C. | 1 in 11·5 parts at 16° C. |
| Solubility of base in alcohol .. .. .. | — | 1 in 362 parts at 17° C. | — | 1 in 324 parts at 18·5° C. | 1 in 102 parts at 16° C. |
| Platinum salt .. .. | Indefinite or decomposed by alcohol. | $2(C_4H_7N_3O.HCl).PtCl_4.2H_2O$. | Indefinite, or decomposed by alcohol. | $2(C_4H_7N_3O.HCl).PtCl_4.2H_2O$. | $2(C_4H_7N_3O.HCl).PtCl_4$. |
| Solubility of platinum salt in water .. .. | — | 1 in 14·1 parts at 15° C. | — | 1 in 24·4 parts at 15° C. | — |
| Gold salt .. .. | $C_4H_7N_3O.HCl.AuCl_3$. Unchanged by ether. | $C_4H_7N_3O.HCl.AuCl_3$. Unchanged by ether. | $C_4H_7N_3O.HCl.AuCl_3$. Decomposed by ether. | $C_4H_7N_3O.HCl.AuCl_3$. Decomposed by ether. | — |
| Reduction of cupric oxide by base compared with that of glucose .. .. .. | 4 molecules $C_4H_7N_3O$ = 2 molecules glucose (after efflorescence.) | 4 molecules = 2 molecules glucose. | 5 molecules $C_4H_7N_3O$ = 2 molecules of glucose (after efflorescence). | 5 molecules = 2 molecules glucose. | — |

Crystallographic measurements of the tabular and efflorescent kreatinins, made by Messrs. L. Fletcher and H. A. Miers, are to be found in the paper, together with full analytical details.

## THE NITRATION OF CELLULOSE.

By F. NETTLEFOLD, F.C.S.

NOTWITHSTANDING that it is now more than forty years since gun-cotton was first made on a manufacturing scale, it still holds its place against the more recent inventions. Lower nitrated celluloses are made on a large scale for powder, and also for pyroxylin. A few remarks on the influence of the nature of the fibre on the condition of nitration may perhaps be not uninteresting to the readers of the CHEMICAL NEWS.

It will be readily understood that the thin wall tubes of cotton fibres are readily penetrated by the mixed acids, and consequently the highest state of nitration results. In the case of ligneous tissue the cells have been thickened by matter from the sap, and almost blocked up. This thick wall is not so readily penetrated, and so only lower nitro-bodies can be obtained.

Thus with clean cotton, using a mixture of 33·3 per cent nitric acid, 1·506 sp. gr. of 94 per cent $HNO_3$, and 66·7 per cent $H_2SO_4$, sp. gr. 1·840, a near approach to trinitro-cellulose is attained,—a product with a solubility of 7 to 9 per cent, having a proportion of nitrogen 13·94 to 13·86 per cent, against a theoretical proportion of 14·14 per cent N in pure trinitro-cellulose, when 0·85 per cent is deducted for ash.

Since so large a quantity of wood pulp is used in the manufacture of powder, such as the Schultze, it may be interesting to consider the few following experiments to show what definite result arises in nitrating these different bodies, though often described—in the case of wood — as consisting of vasculose, para-cellulose, and fibrose.

Beech wood and fir wood are not easily nitrated, on account of the unstable compounds they form. In the case of a fine sample of white pine flour, named O in commerce, a dark ochre-coloured product was obtained with—

41·6 per cent soluble in a mixture of 2 parts absolute ether, 1 part alcohol.
58·4 per cent insoluble in ditto.

The total nitrogen in this was 11·2 per cent.

Taking the soluble portion as being dinitro-cellulose, the insoluble remainder would have a proportion of 11·3 per cent nitrogen, or a rather higher state of nitration.

A sample of wood pulp gave also 11·2 per cent N.

The resinous matter was extracted by boiling in caustic soda, and the washed residual fibre was nitrated, yielding 11·57 per cent N. This proportion of nitrogen would indicate that the product lay between dinitro-cellulose and the formula given by some authors as—

$$C_{24}H_{37}(NO_2)_9O_{20},$$

with 11·9 per cent. It might be conceived at first sight that the insoluble portion consisted of a mixture of trinitro-cellulose and unnitrated fibre, but, as a matter of fact, woody tissue is not readily brought to this high state of nitration.

The existence of these more complicated nitro-bodies, with four times the formula $C_6H_{10}O_5$, is further seen in the following instance:—

Cotton was nitrated in weak acid, yielding a product—

33·0 soluble in the mixture of ether and alcohol.
63·5 ,, acetic ether.
3·5 insoluble.

Taking the 33 per cent as containing 11·1 per cent N, as dinitro-cellulose, the 63·5 per cent would have 10·1 per cent; analysis gave 10 per cent. The formula—

$$C_{24}H_{33}(NO_2)_7O_{20}$$

has 10·17 for theory. With—

25 per cent nitric acid
75 ,, $H_2SO_4$ } 10·47 per cent N.

20 per cent nitric acid
80 ,, $H_2SO_4$ } 8·23 per cent N.

The latter product might be near to the $C_{24}H_{35}(NO_2)_5O_{20}$, with 8·02 per cent N.

With the mixture of strong acids—

33·3 $HNO_3$,
66·7 $H_2SO_4$,

and various quantities of water, ranging from 10 to 15 per cent, to form collodions, products ranging from 10 to 11·1 per cent nitrogen are obtained: these are all soluble in acetic ether, and are probably homogeneous chemical products.

In the Schultze powder the nitrated wood fibre has 10·44 per cent N lying between—

$C_{24}H_{33}(NO_2)_7O_{20}$ and $C_{24}H_{32}(NO_2)_8O_{20}$,

or between 11·1 and 10·17 per cent. But in order to obtain this in the case of cotton, a dilute acid is required, whereas in the case of wood fibre the strongest has to be taken.

## NOTICES OF BOOKS.

*Colonial and Indian Exhibition.—Reports on the Colonial Sections.* Edited by H. Trueman Wood. London: Wm. Clowes and Sons, Limited. 1887.

It was originally intended to confine the Reports of this Exhibition to the consideration of raw products only, or such manufactures that might be of importance to trade between England and her Colonies. A few exceptions have, however, been made in the case of some exhibits which appeared to be of special interest.

The first report is on Mining Industries, by C. Le Neve Foster, and is, owing to the vast mineral resources of our possessions, of very great importance. The collection of metallic ores, coal, and other minerals, was an extensive one, and attracted a good deal of attention from visitors to the Exhibition. In these pages we find the exhibits of each colony thoroughly described, giving even a better idea of their diversity and value than could be obtained by a mere inspection.

The supply of grain is a question which is of universal interest. Wheat, which has been called "the king of grains," is the principal food-stuff of our race. Its cultivation of late years has increased so enormously abroad that it no longer pays the farmer to grow it at home. Canada, our oldest colony, is the first examined in this report, but it does not appear that the export has yet reached a very large total: much is, however, expected in the course of a few years from Manitoba and the North-West Territories.

Victoria has been making rapid strides during the past fifteen years, during which period the land under cultivation has been trebled in extent. Since 1877 Victoria has exported wheat regularly, and in some years largely, but is beaten by South Australia, whence wheat has been exported since 1850, and last year to the amount of 1¼ million quarters.

Passing over tea, coffee, sugar, &c., we come to wines, spirits, and such like. New South Wales is said to possess "districts of sufficient area, and combining the necessary conditions of soil, climate, and aspect, to produce wine enough to supply the whole of the world." The vine is not indigenous to Australia, but being imported in 1820 it flourished and multiplied, and the wine-making industry is now assuming considerable importance.

The Cape of Good Hope is far earlier in viticulture than the Australian colonies, the cultivation of vines having commenced there about the year 1653. Between 1880 and 1885 the number of vines increased from 60 to 70 millions.

The report on Drugs, and Chemical and Pharmaceutical Products, is more of a catalogue of the articles exhibited; but interesting notes are found on *Cinchona Bark* and other exhibits.

Wool, silk, and timber are three raw materials of very great importance. The silk from South Australia is very favourably spoken of as being superior to that from China and equal to Japanese or Italian. That from the other colonies is also praised, and the continued search for indigenous species of silk-producers is strongly urged.

The whole volume from cover to cover is of extreme interest, and it is a difficult task to say which colony is the most valuable; all have their special advantages, and all are progressing.

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*On Forecasting the Weather.* By B. G. Jenkins. Brussels: F. Hayez. 1877.

Forecasting the weather is a question which interests everybody, no matter what his occupation may be; and it may be safely asserted that, no matter what weather we have, there are sure to be thousands of persons who will grumble and find fault with it.

Of recent years the science of forecasting has been vastly improved, the improvement being principally due to the rapid communication between one station and another by means of the electric telegraph, but, even with this at the disposal of our meteorological department, it is not very uncommon for the results to be hopelessly different from the weather expected.

The boldest idea in this direction is undoubtedly that now put forward by Mr. Jenkins. He professes to forecast the weather of any year simply by knowing what it was sixty-two years ago. He says:—"By a process which it is not necessary for me to enter into now, I have found that the barometric and thermometric readings for London, for this year 1887, will be practically the same as those which have been recorded for the year 1825." In proof of this statement he gives charts of the pressure and temperature for the same months in these two years. With regard to the temperatures we admit that there is a great resemblance, but one year is so like another that we cannot admit the proof, while the curves of barometric pressure seem to us to be very far from coinciding. The cause of this alleged similarity is, Mr. Jenkins tells us, the position of the moon. But on examining the charts carefully we cannot come to any other conclusion than that the moon has little or nothing to do with it. How is it possible that the moon can affect the temperature of a day in June, or the rainfall of the month of January? these being cases in which a similarity exists. The moon might possibly have some influence on the height of the barometer, in somewhat the same way as she produces tides, but it is precisely in this case that a want of agreement occurs.

One more point we cannot pass over in silence. Mr. Jenkins attributes some of the differences between two years which *ought* to agree "to inequalities in the moon's daily motion."

---

*Technology Quarterly.* Vol. i., No. 1. Massachusetts Institute of Technology, Boston.

A large amount of work done by the advanced students of the Institute having no regular channel for publication, it was thought that this new Journal would be an excellent medium for recording the original researches and investigations carried on by them. The contents of this, the first number, are of a most varied character, comprising chemistry, engineering, physics, electricity, biology, &c.

The paper describing a method for calibrating a thermometer at many points is of considerable interest. Most methods which have been used are only applicable for obtaining corrections at considerable intervals; but the method here described has been devised so as to obtain corrections for very short intervals, and to avoid the accumulation of errors which previously made the results so unsatisfactory.

A paper on the constitution of benzol will be read with

interest by all chemists, as the subject is still attracting a good deal of attention. The author has brought together all the most important facts bearing on the structure of benzol which are to be found scattered through the chemical literature of the last twenty years. He also reviews some of the symbols which have been suggested to represent it. Those which have received the most attention from chemists are the three proposed by Kekulé, Claus, and Ladenburg. After stating a certain number of facts of a chemical nature, such as the formation of benzol from ethylene, the conversion of benzol to trichloracetacrylic acid, &c., and others of a physical nature, such as the heat of combustion of benzol and the molecular volume of aromatic compounds, he goes on to considerations of a more general nature and discusses the different symbols separately, and concludes that what is known as the hexagon symbol is best in accordance with the facts observed; he also thinks that more attention might be given to the Dewar symbol, there being one or two facts which are better explained by this than by Kekulé's, although there are others with which the reverse is the case.

## CORRESPONDENCE.

### DETECTION OF ANNATTO IN BUTTER.

*To the Editor of the Chemical News.*

SIR,—In giving a method for the detection of annatto in buttsr (CHEMICAL NEWS, lv., p. 49) I recommended testing the filtered fat, and that is a good plan when the commercial "butter colours," containing annatto colouring-matter, dissolved usually in some oil, are employed. I have, however, recently met with a butterine which gave only a very faint annatto reaction from the filtered fat, while the unfiltered fat, decanted from the water, salt, and curd, and tested as I have directed, gave a fine reaction. I noticed that the filter-paper through which the fat had been filtered assumed an orange-red tint, and on extraction with ether I got an annatto reaction from this paper.

Evidently in this case the annatto had been employed in the solid state, and much of it had not been dissolved in the fat, so that it would be well to test the clear unfiltered fat for annatto in such a case.—I am, &c.,

H. B. CORNWALL.

John C. Green School of Science,
College of New Jersey,
Princeton, June 8, 1887.

### SOFTENING MAGNESIAN WATERS.

*To the Editor of the Chemical News.*

SIR,—The note by Mr. Wanklyn, on the above, which appeared in CHEMICAL NEWS, lv., p. 276, will lead many to believe that an analyst can frame his report so as to suit either side of a legal question.

This is no compliment to our profession, or to the common sense acumen of a parliamentary committee.

Having had a great deal to do with Clark's process of softening water, I am able to confirm Professor Frankland's opinion, so far, "that the Clark's process is not applicable to waters containing a large quantity of magnesia."

A great deal will depend on the form in which the magnesia exists in the water. Accepting the tabulated analysis of the Sudbrook water, as given by Mr. Wanklyn, as correct, we may predict that 5·4 grains carbonate of magnesia may be removed, *at least to some extent*; this will leave 6·4 grains magnesia salts, which are readily soluble and not so easily removed.

It is a well-known fact that lime water may remove the carbonates, lime, and magnesia which exist as such, by the removal of free $CO_2$. Now as to the other magnesia compounds, assuming that lime water, if added in large excess, may remove them, we have to contend with the important fact that the corresponding lime compounds are formed, which are soluble, and consequently the improvement of such a water is problematical.

Mr. Wanklyn says that Mr. Porter has no difficulty with magnesian waters; as I am interested in this matter, perhaps Mr. Wanklyn or Mr. Clark will say how 300,000 gallons of a highly magnesian water could be softened per diem, and otherwise manipulated so as to be fit for use.

Is Clark's process in use for softening a highly-charged magnesium water in which the magnesia exists in other forms than carbonate? and is there any other analysis of the Sudbrook water which confirms that given by Mr. Wanklyn?

The atmosphere of a committee room may be so vitiated with chemical fog, in the form of scientific conflict, that one can hardly wonder at a water bill being defeated. I know for a fact that scientific experts are looked upon with suspicion by jurists.—I am, &c.,

THOMAS T. P. BRUCE WARREN.

Tamworth Villa, Earlham Grove,
Forest Gate, E.

### IMPROVEMENTS IN CHEMICAL ANALYSIS.

*To the Editor of the Chemical News.*

SIR,—The interesting article (CHEMICAL NEWS, vol. lv., p. 287) describing the advances made in chemical analysis during the past fifty years omits one method of examination which I think deserves mention. I allude to the principle of proximate analysis by the use of immiscible solvents. This method of separation has been carefully studied by Dragendorff and others, and is simply indispensable in proximate organic analysis.—I am, &c.,

ALFRED H. ALLEN.

Sheffield, June 25, 1887.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. civ., No. 22, May 31, 1887.

**Certain Crystalline Alloys of the Platinum Metals and Tin.**—H. Debray.—An alloy of platinum and tin is obtained by the action of a very dilute acid upon a mass containing about two per cent of platinum. It forms brilliant laminæ, the composition of which answers to the formula $PtSn_4$. The rhodium compound is not attacked in the cold by concentrated hydrochloric acid, and is easily obtained in small brilliant crystals of a fine metallic lustre. Its composition is $RSn_3$. The iridium and ruthenium alloys have a similar composition. Osmium does not form an alloy with tin.

**Reproduction of a Sodium Carbonate known as Urao and Trona.**—Paul de Mondesir.—The "urao" of Boussingault agrees in composition not with the sesquisalt, but with a $\frac{1}{3}$ carbonate, which the author has produced artificially.

**Action of Selenious Acid upon Manganese Dioxide.** — M. Laugier. — The author's researches show that selenious acid, when acting upon manganese peroxide, seems to produce, in the first place, a selenite of manganese peroxide, which, on decomposition, yields different manganese sesquiselenites. Selenious acid is not oxidised

directly by hydrated manganese dioxide, and when such oxidation ensues it forms a secondary decomposition-product.

**Hydrates of Barium Chloride.**—H. Lescœur.—This paper does not admit of useful abridgment.

**On the Chromo-iodates.**—A. Berg.—These salts appear generally as crystalline crusts, and rarely as distinct crystals. They are decomposed by water, which tends to split them up into iodates and free chromic acid. This decomposition is limited, and is arrested by the presence of an excess of chromic acid. The chromo-iodates, if hydrated, lose their crystalline water at 120° to 140°. On a further rise of temperature, oxygen and vapours of iodine are given off, and a dichromate remains. The solutions of these salts are acid. They easily yield oxygen to reducing agents. With sulphurous acid and hydrogen sulphide they yield hydriodic acid, chromium sesquisulphate, and a sulphate of the base of the salt. The author describes chromo-iodic acid, and the potassium, ammonium, sodium, and lithium salts.

**The Constitution of Clays.**—H. Le Chatelier.—The author, continuing his study of the clays as regards their behaviour with heat, arranges them in five groups: the halloysites, the allophanes, the kaolins, the pyrophyllites, and the montmorillonites.

**On a New Betaine, Trimethyl-α-amido-butyro-betaine.**—E. Duvillier.—This compound is produced by the reaction of an alcoholic solution of trimethylamine in excess (1·5 mols.) upon 1 mol. bromobutyric ether. The new compound is very soluble in water and in alcohol, insoluble in ether, and has a neutral reaction. Its chloro-platinate appears in elongated orange-yellow crystals, scarcely soluble in alcohol. The behaviour of the chloro-aurate is curious. On treating the solution of the hydro-chlorate with gold chloride there is formed a sort of a yellowish white precipitate, which is the emulsion of a heavy yellow oil. On boiling this oil dissolves in the water, but on cooling the liquid becomes turbid and the oil reappears, but after some hours there are formed laminar crystals, and soon the oil itself is transformed into crystals.

**On Two Isomeric Mono-nitro-camphors derived from Ordinary Camphor.**—P. Cazeneuve.—In the transformation of chloro-nitric camphor under the influence of copper, zinc, or iron (see *Comptes Rendus*, 1886, July 16), the author recognises two distinct isomers, the properties of which are here given.

**Simplified Calcimeter.**—A. Bernard.—This memoir will be inserted in full.

**A Contribution to the Study of the Soil of Tunis.**—H. Quantin.—The combined nitrogen in these soils ranges from 0·11 grm. per kilo. to 1·65. The phosphoric acid fluctuates from a minimum of 0·084 grm. to 1·700 grm. The chief deficiency is generally in phosphoric acid, a fact which gives greater importance to the deposits of phosphates discovered by M. Thomas.

*Journal für Praktische Chemie.*
New Series, Vol. xxxv., Part 4.

**Researches on the Relations of Equilibrium in Aqueous Solutions.**—Th. Thomsen.—In this third treatise the author considers the action of soda upon certain normal salts of sodium. He examines the behaviour of soda with sodium tartrate, and finds that by means of a large excess of soda it is possible to show the existence of a lævo rotatory compound; further, he investigates soda with sodium malate, quinate, and camphorate.

**Contributions to the Chemistry of Manganese and Fluorine.**—Odin T. Christensen.—The author has studied potassium chromifluoride in its anhydrous and hydrated form, potassium ferri-fluoride, ammonium mangani-fluoride, the corresponding sodium salt, silver mangani-fluoride, and chloro-purpureo-cobalt-mangani-fluoride. He further discusses the action of the hydrates of the aluminium group upon sodium fluoride.

**A Critique of the Foundations and the Results of the so-called Theory of the Formation-Heat of Organic Bodies.**—J. W. Brühl.—The author shows that the theory of Prof. Thomsen leads to results which conflict with much of our present knowledge of the constitution of organic compounds.

**Preparation of Aconitic Acid.**—W. Hentschel.—The author boils 100 grms. citric acid with 50 grms. water and 100 grms. sulphuric acid from four to six hours with a reflex condenser, and obtains, on cooling, a cake of pure crystals of aconitic acid. This is stirred up with strong hydrochloric acid, poured upon an asbestos filter, and washed to remove all sulphuric acid. The yield is from 35 to 45 grms.

**Action of Phosphorus Pentachloride upon Acetanilide.**—A. Michael.—The principal product, $C_8H_8Cl_2N_2$, forms large white monoklinar prisms, fusible at 116·5° to 117°, insoluble in water, and moderately soluble in cold alcohol.

## MISCELLANEOUS.

**Iodoform as an Antiseptic.**—Iodoform has for so long been looked upon as having antiseptic properties, that any statement to the opposite effect is naturally surprising. Messrs. Heyn and Rosving maintain that these powers have been assumed but not proved, and a long series of experiments made by them brings them to the conclusion that it is not on antiseptic at all. Sterilised iodoform jelly, when inoculated with micro-organisms, was found to be full of them, all growing freely on the third day. One of these jellies was further mixed with iodoform powder, and then injected into the knee of a rabbit; on the following day the rabbit was evidently ill, and the knee much swollen. On the third day some pus was taken from the joint, and from this characteristic pure cultures were obtained.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened or the purpose o giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column he the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

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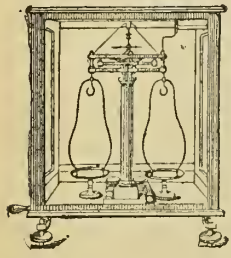

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